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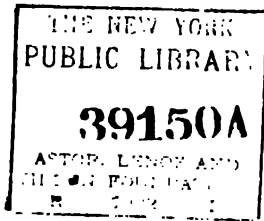
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Contents of Vol. VII, 1893.

Journal of Analytical & Applied Chemistry.

ABNORMAL BUTTER.

BY FRED W. MORSE.

N the course of some feeding experiments during the spring and summer of 1891,[1] two samples of butter were obtained which possessed such abnormal properties that they were not included in the results of the experiments and are here described independently, as one is believed to have yielded a lower figure for volatile acids than any heretofore published.

The first sample was produced by an Ayrshire cow, which had been milked eleven months at the time of the experiment and was then being fed a ration consisting of hay, ensilage, gluten meal and cotton-seed oil. The second sample was from a Holstein cow, which had been milked thirteen months and was then receiving a ration consisting of hay, ensilage, and cotton-seed meal.

The analysis of the samples produced the following results.

<div align="center">

No. 1. Volatile Acids 16.5; Iodin Number 39.6
" 2. " " 11.2; " " 36.0

</div>

The methods which were used in the analysis were those of the Association of Official Agricultural Chemists.

The physical properties of the two samples would have caused them to be condemned by any consumer of butter, as they were very hard, pale in color, and with an odor closely resembling that of tallow. The last property was especially noticeable in the second sample.

There were undoubtedly two principal causes for these abnor-

[1] Bulletin 16, N. H. Experiment Station.

mal qualities, and low figures for volatile acids: the advanced stages of lactation[1] and the cotton-seed products in the food,[2] as these have both been shown to depress the volatile acids, and the cotton-seed meal has been found to reduce the iodin number and raise the melting-point of the butter-fat.

During our feeding experiments, the figures for volatile acids have been found to vary between wider limits than those for the iodin number, both with individual cows and with all the analyses. The following results are from figures obtained with nine individual cows and over one hundred samples of butter. The widest range for volatile acids by an individual cow was 11.2 to 32.4 and the next widest was from 17.6 to 33.1. The widest range for the iodin number, by an individual cow, extended from 30.1 to 44.8, while three other cows had nearly as wide a range. The extreme limits for all analyses, were 11.2 and 33.9 for volatile acids, and 24.2 and 44.8 for the iodin number.

N. H. EXPERIMENT STATION, DURHAM, N. H.,
January, 16, 1893.

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NOTES ON THE INTERFERENCE OF ARSENIC IN THE DETERMINATION OF PHOSPHORUS IN IRON ORES.

BY. E. D. CAMPBELL.

The following tests were made to see to what extent arsenic interferes in the ordinary course of work in making phosphorus determinations. To each of eight students in advanced chemistry, two iron ores were given for the determination of silica, iron, and phosphorus, the last named element to be determined in two portions; first, that soluble in hydrochloric acid, and second, that insoluble in hydrochloric acid; the portion soluble in hydrochloric acid to be determined by a modified method in order to eliminate arsenic. The ores were in most cases different, and each man had with one of his ores 0.100 gm. of arsenic added in the form of potassium arsenate, K_3AsO_4. The method used for the determination of soluble phosphorus was briefly as follows: The ore was

[1] Schrodt and Henzold. Landw. Versuchsstationen. 38, p. 369. 40, p. 309.
[2] Bulletins 13 and 16, N. H. Experiment Station.

dissolved in hydrochloric acid, evaporated to dryness, redissolved in hydrochloric acid, and the insoluble residue fused for insoluble phosphorus and silica. The solution was evaporated down with excess of nitric acid, neutralized with ammonium hydroxid and redissolved in nitric acid. The solution, which is not over sixty cc., is heated to nearly 100° and forty cc. of molybdate solution added. This lowers the temperature to about 55° or 60°, and this temperature is maintained for one hour. The precipitate is then filtered and weighed on weighed asbestos funnels. The method, as modified in order to eliminate arsenic, is essentially the same as appeared in this Journal, Vol. II, p. 370. The arsenic is volatilized as arsenious chlorid by the action of oxalic acid in strong hydrochloric acid solution. This treatment with oxalic acid necessitates two digestions with hydrochloric acid before filtering off the insoluble residue, and this double treatment will slightly increase the amount of phosphorus that goes into solution. For this reason we might expect the per cent. of phosphorus to be a little higher in the first column of the table given below than in the second column. The results given in the table below show the results obtained on the ores to which arsenic had been added. The first column shows the per cent. of phosphorus in solution when oxalic acid was used to eliminate arsenic. The second column shows the amount found when the arsenic was not eliminated, and the last shows the phosphorus remaining with the insoluble residue from the phosphorus given in column two.

As Eliminated.	As not Eliminated.	Insol. P from col. 2.
0.0515	0.0513	0.0024
0.0785	0.0820	0.0005
0.0758	0.1070	Trace.
0.2110	0.2180*	0.0020
0.2180	0.2220	0.0023
0.0545	0.0539	0.0063
0.0843	0.0861	0.0036
0.2086	0.2092	0.0060

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.
February 4, 1893.

MINERALS FROM YORK HAVEN, YORK CO., PA.

By C. H. EHRENFELD.

Altered Stilbite.—There was reported in this JOURNAL, April, 1890, an analysis of stilbite occurring in the trap rock at York Haven. Since then the writer has found other specimens in which the stilbite gradually faded out to a soft (hardness = 2), lusterless, 'white mass without any traces of crystallization. None of this was found imbedded in the rock, but always on a more or less exposed surface. The change is hence probably due to weathering.

Analysis showed the following composition :

$$
\begin{aligned}
H_2O &= 13.57 \text{ per cent.} \\
SiO_2 &= 52.07 \quad \text{``} \\
Al_2O_3 &= 22.11 \quad \text{``} \\
CaO &= 12.17 \quad \text{``} \\
K_2O &= \text{trace} \\
\hline
Total &= 99.92
\end{aligned}
$$

Chabazite.—The mineral was found by Prof. A. Wanner, Superintendent of the York schools, and by him submitted to me for analysis. Following is the composition :

$$
\begin{aligned}
H_2O &= 21.32 \text{ per cent.} \\
SiO_2 &= 50.69 \quad \text{``} \\
Al_2O_3 &= 19.46 \quad \text{``} \\
CaO &= 7.28 \quad \text{``} \\
K_2O &= 1.38 \quad \text{``} \\
\hline
Total &= 100.13
\end{aligned}
$$

Specific gravity = 2.18. Occurs in small, almost cubical rhombohedra, 0.5 mm. to 2 mm. square ; translucent. In respect to gelatinization with hydrochloric acid, this mineral and the two stilbites mentioned above show an exact reversal ; chabazite showed no gelatinization, while stilbite gelatinized freely.

Augite.—This mineral occurs in close proximity to and sometimes mingled with the stilbite mentioned above.

It has a dark bronze green color, shining luster, crystalline

structure and occurs in veins of one to two cm. in thickness penetrating deep into the great masses of trap rock.

Following is the result of analysis :

$$
\begin{aligned}
SiO_2 &= 51.27 \text{ per cent.} \\
Al_2O_3 &= 10.01 \text{ ``} \\
FeO &= 9.11 \text{ ``} \\
CaO &= 13.23 \text{ ``} \\
MgO &= 13.60 \text{ ``} \\
H_2O &= 1.64 \text{ ``} \\
\hline
Total &= 98.86
\end{aligned}
$$

Specific gravity $= 3.008$.

Sphalerite from York, Pa., occurs as a thin coating between the layers of blue limestone in the same quarry with the fluorite which was reported in this JOURNAL, July, 1890. It is light yellow in color and is so thinly spread out that not enough could be obtained free from limestone for quantitative analysis.

YORK COLLEGIATE INSTITUTE,
YORK, PA., Jan. 24, 1893.

DISCREPANCY IN CHEMICAL WORK BY DIFFERENT WORKERS.[1]

BY C. B. DUDLEY, CHEMIST PENNSYLVANIA RAILROAD, ALTOONA, PA.

I have recently seen a series of, I think, sixteen determinations of sulfur in a piece of pig iron, supposed to be the same iron, that differed from each other from 0.005 up to 0.02 per cent., or the extreme results (I am giving these figures from memory) were about as one to four. Now, obviously, while the amount of sulfur is excessively small in this case, not being a matter of very great importance, yet, as bearing on the accuracy of chemical work, the result is something appalling. I have seen a series of phosphorus determinations recently, made by six or seven chemists, where the extreme results differed 0.03 to 0.04 per cent. in a total of about 0.10 per cent. I have a friend, who, for a number of years, was manager of a large furnace, who, some four or five years ago, sent out borings from some pig iron to eight or nine different chemists for phosphorus determination—this is another

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[1] Extracted from an address to the members of the Chemical Section of the Engineers' Society at Pittsburg, September 27, 1892.

case besides the one just referred to—and when he got the results back, no one of the chemists knowing that any other was working on them, they differed almost as one to two; and in his nervous, energetic way, he said: " I said in my wrath, all chemists are liars!" Perhaps it is not necessary to mention any more discrepancies; I might, however, give one more instance. In a recent analysis of bronze, we obtained in our laboratory a trifle over nine per cent of tin; another chemist, working on what was supposed to be exactly the same metal, being half of the same pig, got over ten per cent., the discrepancy being about $1\frac{1}{4}$ per cent. Now, obviously, there is something wrong somewhere. Why is it that we get such discrepancies? Undoubtedly, most of you have reasons quite ready to explain some, at least, of the discrepancies. I have gone over the subject recently, and, as I philosophize, the causes for discrepancy in chemical analyses may be grouped under four heads. You shall say, after I am through, whether there are more; whether I have covered the ground, or have left something out, or whether I have got too much in. I will say, by the way, in order not to mislead you at all, that a portion of what I am about to say has been published recently in an article in the *Railroad and Engineering Journal* of New York; not with the same dilution, perhaps, that I shall give it to you, but the gist of the thought. I wouldn't like to get up here and give you something as original that has once been published.

The first cause of discrepancy in chemical work is that the two chemists did not work on the same sample; or, in other words, non-uniformity of samples. Upon this point, your own experience will doubtless give each of you an illustration. I do not have in mind now anything occurring out of our own personal experience in our laboratory work at Altoona, now nearly seventeen years of it, where there has been serious discrepancy due to difference in sample. The nearest we have come to it is this: At one time we were buying spiral springs on specifications that the carbon should not be below 0.90 per cent. The springs we examined were made out of a steel wire about a quarter of an inch in diameter, the coil being about an inch and a half across, and five or six inches long, what we call "A" springs, and used

to hold the box lids tight to the oil boxes under the cars. We found in those springs so low carbon, in a number of cases, that we rejected them. The manufacturer got some one else to determine the carbon in the steel, and found the requisite amount; and so, of course, the question came up for an explanation as to the discrepancy. The discrepancy was very easily explained, and we ourselves, in our later work, found the same peculiarity in other steels; the borings required for analysis of these springs (they were unhandy, unwieldy things to bore, being small) were simply what we could get handily, mostly from the outside of the wire. The manufacturer took the same springs, had the outside turned off, and then took his sample from the center of the wire, and this was the cause of the discrepancy, as we have proved by a number of test analyses. Apparently the outer layer of a steel rod that has been heated, as is commonly done with spiral springs, very frequently loses 0.10 per cent. of carbon in the fire. Or it may be, segregation during cooling explains the difficulty. At any rate, we have several times done this, *viz.*, take a wire rod, $\frac{3}{4}$ of an inch in diameter, and have the boring done from the side, not the end, with a $\frac{1}{8}$ inch drill, may be $\frac{3}{16}$ of an inch deep, and then make a carbon determination from these borings, and then take $\frac{3}{16}$ of an inch more toward the center and make a second carbon determination; we never get the same carbon in the two samples. This is the nearest to an easy illustration that I can give you of discrepancy due to difference in sample. Of course, it is perfectly obvious that if the samples differ, there is a legitimate and good reason why the analyses should differ. This is especially true of shipments that are made up of large quantities, and are sampled by the single sample. We have many times had this brought to our attention by the men at the shops. Samples taken out of the same lot of material may not show up the same. They say it is the same material because it came in the same car. This is especially true in oil samples. It is not at all rare for a manufacturer who receives an order for fifty barrels of lard oil, for example, not to take that oil all out of the same tank, although he ships the fifty barrels in the same car. We have had a number of cases where the amount in tank did not suffice to fill the order, and, consequently some was taken out of another

tank, and sometimes inferior material was put in—two or three
barrels, as the case might be—to fill the order.   But I need not
go further upon this point.   You will all recognize that there is
a clear and sharp reason for discrepancy in analyses if the samples
are not the same ; and in all our work, when we come to a serious
difference between ourselves and anyone else, we exchange
samples.   That is one of the first things we do,—exchange
samples to see whether the difference lies there.

The second cause for descrepancy in chemical analysis is im-
purity in the chemicals.   I doubt not many of you have run across
this peculiarity.   One of the most recent we ran across was this :
In mixing up some wash water of sulfate of ammonium and free
sulfuric acid for washing the yellow precipitate in phosphorus
determinations, we ran across a very puzzling sort of trouble,
namely, after washing a few minutes the filtrate became turbid,
and the more we washed the more turbid it became; and we
were inclined to think that the published statements of the
insolubility of the yellow precipitate in sulfate of ammonium
and sulfuric acid wash water were probably fallacious ; but on
looking into the matter we found that the commercial sulfate
of ammonium we had used had a little phosphorus in it.

There are many discrepancies in analyses due to the impurity
of the chemicals used, and it is not always an easy matter to say
whether the chemicals are pure or not.   I must say frankly to
you that the longer I work, and the more experience I get, the
more I am inclined not to be so sure as I used to be.   Obviously,
there are two or three methods of checking up whether the chemi-
cals are pure or not.   One of the most common is simply to test
the chemicals; but I do not know how anybody would have
found the impurity by that method, which was run across in the
work of the International Committee on Standards in carbon
determinations, namely, the presence in chlorid of ammonium of
a little organic matter, that only comes out when you dissolve
steel in the double chlorid of copper and ammonium.   Another
method is to make a dummy analysis, using a second beaker, to
which you add only the reagents that you use in the one con-
taining the substance to be analyzed, and then weigh up what
you get from the two, and deduct from the genuine analysis what

you find in the dummy. There is always a little uncertainty in that, namely, have the same reactions taken place in the beaker that has not got the substance in to be analyzed that have taken place in the beaker that has the substance? There is one thing more present in the beaker that has the substance in, and this additional thing may introduce changes in the final result. The dummy analysis is not always quite certain; in many cases it undoubtedly is. I would hardly feel willing to say that you will always catch up the impurities of the chemicals by the dummy analysis, nor would I think that you could always catch up the impurities of the chemicals by a test, as it is so difficult sometimes to test them.

This is a thing that all of us, undoubtedly, need to pay a great deal of attention to. I would like to call your attention to an instance. We had some so-called C. P. molybdic acid from five different sources recently; three of them had ammonia present; one of them was free from ammonia, but there was a little soda or some other soluble base with it; and one of them was pure molybdic acid as far as we could get at it. Such peculiarities as these many times may possibly cause discrepancy. It is evident that in making up a solution of molybdate of ammonia, if you have something called molybdic acid, and put in the amount required of this material, and it is in reality molybdate of ammonia or of soda, you do not get the same strength of solution you would have if genuine molybdic acid had been used. Our experience indicates that this point cannot be ignored in phosphorus determinations. Your own experience will, of course, do two things for you; first, warn you (has already warned you, undoubtedly) never to trust results of analysis unless you have checked up the chemicals, and, second, will convince you that there are many impurities in so-called C. P. chemicals.

A third cause of discrepancy in chemical analyses is what may generally be called "poor manipulation." I know of chemists who think this is the principal cause. The main cause of discrepancy in chemical analyses, some say, is poor manipulation, or lack of skill. My old teacher in chemistry, who has now gone out of the business, and lives on a farm in California, was characterized by this one very remarkable peculiarity, namely, he

never believed anything as long as there was a shadow of doubt and after all known uncertainty had been removed he was not quite sure ; in other words, he was a man who was really a strug- gler for accuracy. He used to say to me in his very dry way, "No chemist can make an accurate analysis. There are chem- ists who can work near enough to accuracy so that their work is valuable. There are chemists who can not. And that is the difference between chemists." Of course, what I mean by an accurate analysis is a question of limits. Some analyses are accurate to a half per cent., some to a tenth of a per cent., and some, perhaps, to a hundredth. of a per cent., but none, I think, are the exact truth.

The point I want to make, however, is not a dissertation on accuracy, but the difference between chemists due to manipula- tion. Undoubtedly, this is a very frequent source of error. I remember very well when I was a student, I was set to make a determination of iron. I dissolved the substance in sulfuric acid with the utmost care, excluding the air, and, at the end of the operation, after going through the necessary routine, I filled up my flask to one liter, shook, and supposed I had a solution that was in every sense what it should be for the subsequent operations, which were to draw out successive portions of one hundred cubic centimeters, and titrate them with permanganate of potash. To my surprise, the first two that came out differed from each other from ten to fifteen per cent. What was the diffi- culty? Why, simply, I had not mixed the materials. I thought in my inexperience, that if they went into the same flask, it was all right if I gave it a shake and a stir. Let me give you another illustration. Recently, we had occasion, in our laboratory, to make some tests for phosphorus, and I set two or three boys at the same thing. We knew pretty well from good careful man- ipulation and fairly well tested methods, what the steel contained, and the directions were to wash the yellow precipitate until the wash water tested with sulfid of ammonia showed no change of color. We were washing out molybdic acid and iron salts, and, as you know, both the molybdic acid and the iron would show change of color with sulfid of ammonium. In some five deter- minations, one of the boys got (it was low steel, containing

almost exactly 0.4 per cent. of phosphorus) 0.048, 0.047, 0.051, 0.043, 0.045. You will note the discrepancy, and yet he had followed the directions, as he supposed, with absolute accuracy.

There are two points involved in this illustration, namely, to show how the manipulation may be at fault, and, also, however accurate you may be in giving directions as to how analyses shall be conducted, you may be thwarted by something you had not thought of. Well, on careful examination, we located the difficulty. The difficulty was simply this; the yellow precipitate had a little tendency to crawl, and .this manipulator was a little bit afraid it would get over the top of the filter, and, possibly, get carried down through with the washings, and in his anxiety to avoid this he failed to wash all the molybdic acid out of the upper part of the filter. He supposed he was washing it out completely, but as the result showed by failing to wash to the top of the filter he removed so little with each successive addition of wash water that the amount was too small to react with sulfid of ammonium, so that although he accurately followed the directions, he still left enough molybdic acid (which you know, by the volumetric method, is what we are really measuring) in the filter to give a little high results.

I have no doubt that hundreds of illustrations will occur to you where manipulation comes in as an element of error. Directions are given, say, for example, to heat to a certain temperature. One man guesses at it; another puts in a thermometer. Again, the directions may be very indefinite. They may be, for example, "add a little of this or that," or "add a little, not too much," without giving any measurements whatever. Or, the directions may be accurate, "add five cc.," or, "ten cc.," and one man guesses at it, and another measures it. The manipulation certainly does affect the analysis. In filtering, one man slops a little, and another does not. All of these are points that come in, so that I think, without further question, you will accept this as one of the reasons why there are discrepancies in analyses, namely, failure on the part of one or the other of the chemists in accuracy of manipulation.

Now there is a fourth cause for discrepancy in analysis, if I understand it rightly, and that is the method. I think you will

all agree, that two methods may not give exactly the same results. I have in mind a couple of cases which occurred quite recently with us. In a determination of tin in bronze, we never weigh up the metastannic acid as we separate it from the bronze by means of nitric acid. We have never succeeded yet in getting all the iron and all the copper away from the oxid of tin by means of nitric acid. Also if the bronze contains any phosphorous, it will, as you know (part of it, at least), go down with the tin. Even if you take an ordinary straight bronze, that is simply a copper-tin alloy, and dissolve it in nitric acid, and weigh the tin just as you get it by separation in nitric acid solution we think your results will be a little high. So we dissolve our metastannic acid in sulfid of ammonium, filter and reprecipitate the tin sulfid ; in this way we always get a little copper out, and sometimes a little iron. And although, as you know, we do not even with this care completely separate the copper from the tin owing to the solubility of copper sulfid in sulfid of ammonium, we think we get much nearer the truth than if we neglected this precaution. On the other hand, I have known cases where it is quite the custom to weigh up the metastannic acid just as it is separated from the other constituents of the alloy by means of nitric acid. Now here is difference of method. No one would think those two methods ought to give the same results.

I have another illustration : We have been accustomed for a little while, to determine the lead in alloys by precipitating lead on one of the poles of a battery as binoxid, according to Edgar F. Smith's recent manual of electro-chemical analysis, a book which, by the way, each and every one of you ought to have and study carefully. I need not give you the detail of the method farther than to say that if you have copper and lead in nitric acid solution and apply the battery, the conditions being all right, the copper precipitates on one pole as metallic copper, and the lead on the other as binoxid. If we may trust our experience the results are excellent, if you have nothing else but copper and lead present. We took a known amount of lead and put in with it a known amount of copper, and get out almost the actual amount we put in, so that we think the method is capable of great accuracy. But in a recent analysis of a bronze containing lead

we got one per cent. higher in lead than somebody else got by the
sulfuric acid method, and the worst of it was that when we
came to determine the lead by the sulfuric acid method, we
confirmed the other chemists' results. It took a little time to find
out where the difficulty was. I may say, for your information,
that bismuth follows the lead, if it is in small amount; if it is in
large amount, it will go with both the copper and the lead. We
found a trace of iron in with the lead, and just the faintest trace of
copper, a little tin, a trace of antimony, and strong suspicions,
but not positive proof, of bismuth, apparently enough, in the
aggregate, to account for the discrepancy. So we see that all
methods of procedure are not equally good. All methods will
not give the same results. "Method," therefore, is a fourth cause
of the discrepancies in chemical analyses.

Now, if you will forgive me, I would like to spend just a mo-
ment on another thought that comes in perhaps under manipula-
tion best, but almost seems worthy of a place by itself, namely,
there is frequent discrepancy, if we may trust our experience in
chemical analysis, due to the fact that one chemist knows what
he is doing, and the other chemist simply follows directions and
doesn't know what he is doing. I have seen a good many chem-
ists make chemical analyses whose minds seemed to be anywhere
else except upon the analysis; whose minds did not follow the
changes that were taking place; who did not understand the
rationale of the process. I have seen other chemists whose minds
were always engaged upon the changes that were taking place
while they were making the analysis, even during the filtration.
One thinks, "What are we washing out?" The other thinks
only, " the book says, wash," and so he goes ahead and washes.
He doesn't think what he is washing out; and usually doesn't
test to see whether he has washed it all out or not, unless, perchance,
the book especially says so; he is thinking of something else.
We had an illustration of this lack of thinking what is going on
in the progress of an analysis which caused us a little annoyance
recently. This very puzzling thing happened to us: We made
an analysis of a tire and found about 0.14 per cent. of silicon in
it. The analysis was made by the Drown method, dissolving in
sulfuric and nitric acid, evaporating until the sulfuric acid fumes,

and then diluting with hot water and filter.   You are doubtless all familiar with the manipulation.   As I said, we found 0.14 per cent. of silicon in this tire.   About a month after it was sent out we received a letter from a chemist of another railroad, saying that he had seen the analysis that we made of the tire, and that his determination of the silicon in the same tire was nearly double ours, and asked us to kindly send him our method so that he could check himself up and see where he was wrong.   He was very nice about it, you see.   Before sending him the method we thought we would go over our own work again, and upon doing so, confirmed his results.   I would like to say here, in parenthesis, that the average of our work does not cause us this trouble.   We make a great many hundreds of analyses, and these are only a few cases, but they happen to illustrate my re-marks, and it is better that I should draw my illustrations from my own experience, if possible.   Where was the difficulty ?   Our subsequent work, I say, confirmed the analysis of the other chemist ; we got 0.28 per cent., same as he did.   On looking the matter over we found the difficulty.   A great deal of work is done in the Pennsylvania Railroad laboratory, and much of our work is the examination of shipments of commercial products that are bought for use on the road.   Now, other people's actions depend on the results of our work.   If, for example, we buy a shipment of 100 barrels of oil, none of that oil can be used, unless some very great emergency has arisen, until the laboratory report is furnished to the parties who are to use it, so that we must not allow anything, unless it is very serious, to interfere with our doing that work.   It happens, therefore, that the work on ship-ments takes precedence, and the investigation of miscellaneous samples takes our leisure time when we are not working on ship-ments.   This was the case with the tire.   The operator who had the matter in charge, apparently without thinking exactly what he was doing, since he was doing a great deal of other work, and had many irons in the fire, dissolved the steel in the regular way, evaporated to the fuming point (just as he should have done), but, then, instead of diluting with hot water and filtering at once, he diluted and let it stand.   It happened it stood forty-eight hours.   Now, it is possible that none of us would have thought

that this would cause any trouble, but subsequent experiment showed that this was the explanation of the discrepancy. Apparently, the silicon obtained by the sulfuric acid method is not dehydrated completely. At any rate we made positive determinations subsequently on the self-same tire, and if we allowed it to stand forty-eight hours after dilution we lost about half of it. If we allowed it to stand six days we only got 0.06 per cent. I said to our boys that I was glad the thing had happened, because it brought out a point we would not have thought of easily otherwise. Nevertheless, it seems to me that a chemist who thinks much, and who carries his work with him, and understands what is going on, would have thought that possibly there might be danger in the delay.

Now we come to perhaps the most important point in our whole talk, *viz.*, How shall two chemists who differ check each other up? or, come to an agreement with each other? I answer, Where two chemists differ, and the difference is due to working on non-uniform samples, or, on not exactly the same sample, the matter is easily checked up by changing samples. Also, differences due to impurity of the chemicals are not very difficult to check up, either by checking up your chemicals or by the dummy. Sometimes, it is true, the differences due to impurities may be very abstruse and hidden, and difficult to find; but by changing chemicals, as we have done a number of times, you can frequently locate the difficulty. Also, still further, where manipulation is at fault, it is not a very difficult thing for the two manipulators to get together and work in the presence of each other, as is frequently done I understand in Colorado, in assaying. One of my assistants is an old assayer from Colorado, and tells me that, many a time, he and the works' chemist or assayer have worked in the same muffle, side by side, and under the same conditions, so that each could watch the other. Many times it is not necessary to go as far as this; simply talking over the manipulation will show wherein the difficulty lies. These three difficulties—or, rather, discrepancies due to these three causes—are not very hard to overcome; but, here comes the poser. Suppose that the difference is due to method, and suppose that I say I have used a good method, an approved method, a

published method that is recommended, and you say the same in regard to your method, who is going to decide between us? Both of us are, perhaps, a little obstinate, and both of us perfectly right in the position we have taken. If both of us have used regular, well-recommended methods, who is going to decide between us?

Before answering, let us see what is the necessity for a decision. Oftentimes a good many thousand dollars depend on our work. If we make a mistake by using a bad method, or a wrong method, it may mean a good many thousand dollars to somebody whose product we have rejected. He may have to pay the return freight and have the product sent back on his hands; and, as it doesn't pass specifications, he may not be able, without serious loss, to sell it. On the other hand, if the chemist on the other side has used a bad method, we may have to accept inferior material. As you know, more and more every day, large commercial transactions are based on chemical analyses, and differences between chemists may mean thousands of dollars.

We have proposed the following method for overcoming this difficulty. I do not know that it will be approved by the profession, but we do not see any other way out of it, and many chemists and managing men of the different mills whom we have consulted on the matter, have approved the suggestions we have made. The method is simply this: Publish the method we use, and make it a part of the specifications. For example, suppose we are buying spring steel on specifications that it shall not contain over 0.05 per cent. phosphorus. Now we will suppose that I use the volumetric method, another man uses the acetate method, and we get different results, who is going to decide between us? We have either got to leave it to some third party, and agree to abide by his decision, or have the same method. Now, everybody knows that it is impossible to run a large commercial laboratory on the acetate method for determining phosphorus; it is too slow; and also on the other hand, it is claimed that the volumetric method is not quite so accurate as the acetate method. Perhaps I shall have something to say about that some other time. But, what are we going to do? We simply say this to the manufacturer: "We want steel for springs that shall not contain over 0.05 per cent. of phosphorus, and the phorphorus

shall be determined in a given way. Whatever you find by this method, that is the amount of phosphorous so far as our transaction goes." We see no other way out of this difficulty. Now, let us see; this is a pretty bold assumption; the chemist of the Pennsylvania Railroad Company assumes to dictate to the profession what methods they shall use. Yes; but only for transactions in which the Pennsylvania Railroad is involved. Use any method you choose for your own work; we do not assume to dictate to you a particle; but, as a means of avoiding the difficulty due to difference of method, we simply say to you, arbitrarily, that this is the method that must be used to determine the phosphorus, for example, in transactions where the Pennsylvania Railroad is involved. If we had a standard method, or if any learned society will give a method which shall be regarded and accepted by chemists as final, we will bow to it instantly; we will adopt anybody's method, if it is applicable. We claim no especial originality; we simply give you the method which we use.

Now let us see what is going to come of this. We prescribe a method which shall be used for determining phosphorus, carbon, silicon, sulfur, or whatever it may be. The method as we use it will give certain results; the other chemist will get the same results—at least, we assume that he will. The Pennsylvania Railroad Company puts an upper limit on phosphorus, since phosphorus is injurious to steel,—that is to say, the phosphorus must not go above so much; the interest of the railroad company is to have a method that gives as high results as possible so as to keep phosphorus down; the steel works' chemist, on the other hand, desires that the method in his hands shall show that the steel is low in phosphorus, because if it gets above a certain amount, it is rejected. In other words, the two parties are on opposite sides of the method. It is one's interest to have a method that will cause the rejection of the steel if it is high in phosphorus, and the other wants a method that will make the steel pass. Now, my experience is that in anything where men's pockets are involved on opposite sides of a question, you are pretty apt to get at the truth sooner or later. This is going to bring a criticism of the method of determining phosphorus by the parties in

antagonistic interest.   Our thought is this: The method we send
out to-day is entirely subject to revision; if any one of you finds
a hole in it, say so, and the change shall be made just as soon
as we can make it, providing your work is confirmed.   It is not
our method; it is a method to be used to decide certain chemical
questions.   Our hope is that there will be enough criticism by
these parties in antagonistic interest on the various methods put
forth, so that sooner or later there will result a method which we
will all be willing to accept as standard.   It may be that the
work of fifty chemists will be required before we get such a
method.   There is no assumption on our part of superior know-
ledge; no desire to dictate in any shape or form to the profession;
but we have a difficulty to meet, and we connot see how to get
out of it in any other way.

I asked Prof. Langley what he thought of it.   He said he
thought that some learned society should approve the method.
Per contra, a member of the American Chemical Society is re-
ported to have said that he would bitterly oppose any attempt
on the part of that Society to sanction any method.   He did not
think any learned body should sanction a method.   On the other
hand the agricultural chemists of this country, as I understand
it, have done this very thing, namely, they have agreed that in
the analysis of fertilizers whatever phosphoric acid is shown by a
certain method, which they defined in convention, shall be called
" soluble " phosphoric acid, and the amount of phosphoric acid
that is shown by another method or modification shall be called
the "reverted " phosphoric acid, while the amount of phosphoric
acid shown by still another method or modification shall be called
"insoluble " phosphoric acid.   The method was first proposed
five or six years ago, has been modified three or four times, and
now nearly all the agricultural chemists in the United States, if
I am right, are determining the phosphoric acid in fertilizers by
the method adopted by the agricultural chemists in convention.
If some convention would take this work off our shoulders, we
would be delighted.   We assume it only because we do not know
how to get along and meet our difficulties any other way.

Note by the EDITOR.—The method of determining phosphorus referred to by Dr.
Dudley in the above article will be given in full in our next issue.

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Zymotechnisches Centralblatt.   Referirendes Organ über die neuesten wissenschaftlichen Forschungen und praktischen Erfahrungen auf dem Gesammtgebiete der Bierbrauerei, Spiritusbrennerei, Malz- und Hefefabrikation, redigirt von E. Wein.   München, 1892.

THE CONSTITUTION OF MAGNETIC OXID OF IRON.[1]
BY W. G. BROWN.

After considering the views of the constitution of magnetic oxid of iron held by different chemists, Emmens' gives a graphic formula for it which is regarded as fully accounting for its physical behavior.   In the same paper graphic formulas are furnished for ferric and ferrous oxids which explain the chemical behavior of the magnetic oxid more in accordance with the commonly re-

[1] "On the Constitution of Magnetic Oxids."   This Journal, 6, 583 et seq.

ceived views, and, at the same time, show three atoms of iron united.

Take the graphic formula (*l. c.*, p. 588).

$$O = Fe \overset{\displaystyle \diagup O \diagdown}{} Fe = O$$
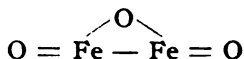
this by union with (*l. c.*, p. 587)

$$= Fe = O$$

becomes

$$O = Fe \overset{\displaystyle \diagup O \diagdown}{-} Fe - Fe = O$$
$$\overset{\|}{O}$$
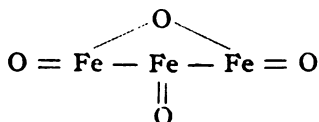
which agrees with Emmens' conditions, for "each molecule (atom) of Fe is quadrivalent and each molecule (atom) of O is bivalent."

By this formula the molecule has a constitution in which the Fe of the Fe_3O_4 can easily be imagined as separating into the different states ordinarily called ferrous and ferric and forming such salts when acted upon by a non-oxidizing acid. And here it may be said that all that is meant by these terms is that all the atoms of Fe in Fe_3O_4 do not behave alike.

To objection sixthly (*l. c.*, p. 586) may be used the words of the paper, "we also see here that a polymeric form is possible," viz.,

$$O = Fe \overset{\displaystyle \diagup O \diagdown}{-} Fe - Fe = O$$
$$\diagup \diagdown$$
$$O \quad O$$
$$\diagdown \diagup$$
$$O = Fe - Fe - Fe = O$$
$$\diagdown O \diagup$$

or

$$O = Fe \overset{\displaystyle \diagup O \diagdown}{-} Fe - Fe = O$$
$$\diagup \diagdown$$
$$O \quad O$$
$$\diagdown \diagup$$
$$O = Fe - Fe - Fe = O$$
$$\diagdown \diagup$$
$$O \quad O$$
$$\diagdown \diagup$$
$$O = Fe - Fe - Fe = O$$
$$\diagdown O \diagup$$
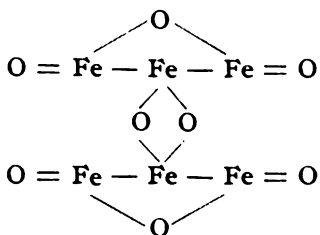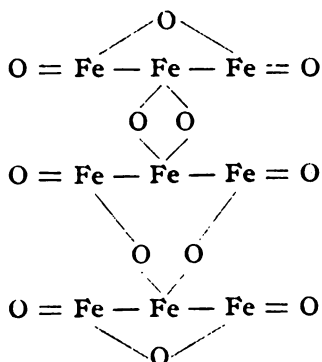
and so on.

To objection fifthly (*l. c.*, p. 586) the compound Fe,O,,6SO, (omitting the H,O) may be written graphically:

$$O = S - O - Fe - Fe - Fe - O - S = O$$
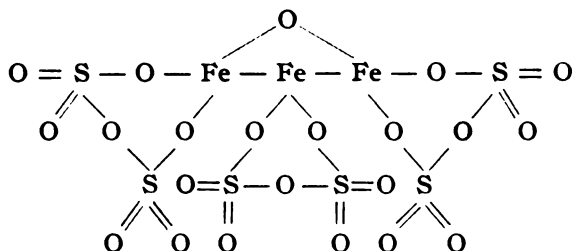
With regard to the statement (*l. c.*, p. 587) ''let us recognize the fact of the magnetic property of iron being impaired and well nigh destroyed by the union of the metal with oxygen; a fact which leads us to conclude that in any strongly magnetic oxid of iron some part at least of the metallic molecules must exist uncombined save with iron,'' it must not be overlooked that it is only a half truth. Oxygen has recently[1] been shown to be strongly magnetic, so that we might say the magnetic property of oxygen is destroyed by its union with iron. The true explanation of the magnetic property seems to be that of the paper (p. 586) that ''magnetism is * * a physical property, dependent upon the molecular structure.'' This being granted we have offered the formula suggested by Emmens' paper as a better explanation of the chemical and physical behavior of magnetic oxid of iron than the one there given.

WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VA.

TRINIDAD PITCH: ITS OCCURRENCE, ORIGIN, NATURE, AND COMMERCIAL APPLICATION FOR PAVING.

BY CLIFFORD RICHARDSON.

At Hadley's Diggings, 1,200 feet northeast of the lake, just off the village road, the changes in the nature of the pitch become very apparent, at least to an expert observer. The soil covering is more than three feet thick. Cokey and iron pitch

[1] Am. Jour. Sci., 44, 420.

are found, together with the chocolate-colored oxidation products of the latter. As we move on the deposits become more and more scattered in detached masses through the soil, and the proportion of pitch to excavation generally smaller, although at the Point and in some of the village lots large masses have been found.

In these deposits it occurs in all manner of forms, as I have described. It is thrown out of the pits, collected in heaps, and then gone over by hand by gangs of negroes, who sort out the best portions and trim them with cutlasses, removing the cokey and chocolate portions and the iron pitch. It is then considered suitable to be hauled to the beach for shipment or to be stored in piles. Formerly there was much less care taken in this respect, and much very inferior stuff reached us, but since the condemnation of the *Teneriffe* cargo, and the subsequent competition between lake and land pitch, there has been a vast improvement in the land pitch exported. In addition, some of the excavations are now nearer the lake than formerly and the pitch in consequence is better than that originally taken from the lots on the Point and near the water.

The hauling and loading of the land pitch is done in much the same way as that of the lake. On the beach at La Brea, when I was there, there were seven piles, one of lake pitch belonging to the Trinidad Asphalt Company, and the others of land pitch, belonging to Turnbull, Stewart, and Co., Carter, Hawley and Co., Pine, or the West Indies Asphalt Company, and to one or two men who collect and sell it to shippers for whatever they can get.

AVAILABLE LAKE PITCH.

Practically the whole of the lake deposit is available, since any excavation is soon filled up by the natural process of other pitch flowing in. How much pitch the lake contains has been a matter of much conjecture, but as there is no knowledge of the depth of the deposit nothing definite can be told in regard to it. The deposit is plainly not inexhaustible, since the removal up to the present time of less than a million tons has produced a depression of the level of the surface of about a foot.

AVAILABLE LAND PITCH.

Various estimates have been made of the area of land pitch available and of the amount which can be excavated. Messrs. Finlayson and Co., reliable authorities, state that at a rough calculation there may be about 12,000 acres on which more or less asphalt may be found. Of these about 11,000 belong to or are controlled by the Trinidad Asphalt Company ; the Government have about seventy acres; Turnbull, Stewart, and Co. control about twelve acres; the Countess of Dundonald has about six acres; Behi court one acre; Espenet one; and there are about five acres in small lots. The undisputed land outside of the Crown and Trinidad Asphalt Company has been partially exhausted and would not probably yield now, they say, more than 6,000 to 8,000 tons per annum for four or five years. This estimate is under date of tenth of May, 1892, and does not seem to include the Mon Repos lot of twelve acres thrown open by decision of the court. I am inclined to think this must be much underestimated, but it depends largely upon the outcome of the disputes before the courts over land claimed by the land pitch workers from the Trinidad Asphalt Company and the Crown.

Mr. Carl Boos, of the firm of J. N. Harriman and Co., informs Consul Pierce as follows:

" While it would be too speculative a matter for me to estimate the probable yield of the asphalt deposits on private land, I may say without fear of contradiction that several hundred thousand tons might easily be won from them annually for a good number of years, the more so as the deposits are being continually replenished. I know of several lots where this was proved beyond a possibility of a doubt, in one instance particularly, where a pit thirty-two feet deep, from which about 8,000 tons had been taken, filled up within five or six months, the ground becoming almost level with the surface. The private lands I refer to do not belong to the Crown or the Trinidad Asphalt Company."

Such conflicting opinions form no basis for any reliable estimate of the amount of land-pitch available, but from my own observation and knowledge I believe that when with the reorganization of the courts of justice in Trinidad the concessionaires are given such protection as seems due them the amount exported will be largely decreased.

LAKE AND LAND PITCH—THEIR PROXIMATE COMPOSITION.

For the purpose of studying the various deposits of pitch and making a comparison of their properties and value for paving purposes, a large collection of specimens was made from the lake and from the land deposits. These have been carefully examined since my return and the results are presented here, together with some observations upon commercial specimens collected in this country which have extended over a number of years.

On the lake, specimens were collected at each station on the line of levels, which was run from north to south across it at intervals of 100 feet, and also on an east and west line at infervals of 200 feet, and at the soft and semi-soft spots.

Specimens of land pitch were taken from the several excavations which were visited, from the heaps prepared upon the beach for shipment, and in a few places where the pitch is not worked commercially.

The samples were brought to this country in tin boxes, and although most of them less than a pound in weight represent, I believe, fairly the deposits from which they were taken. Some of the better class of land pitch deposits had not been opened when I was in Trinidad, but of one or two of these I have since obtained specimens.

The results of my examinations are given in Table I.

The general appearance of all the samples from the lake is the same, except that of the soft pitch. They present that porous, live, and more or less moist character for which, as I have said, the pitch from the lake is noted, and although at the edges the surface is more or less dry and scaly, the pitch is found at a short distance below to be normal. This similarity of appearance is accompanied, as an inspection of the preceding analyses shows, by a very great uniformity in composition. The average composition of lake asphalt, and the extremes which were found, excluding the soft and medium soft portions near the center, is as given in Table II.

In considering these results, it must be remembered that the amount of water found may in some cases be somewhat smaller than the true amount originally present in the pitch, as it slowly dries out, and is very liable to do so during the transportation and

TABLE I. LAKE PITCH.

Serial No.	Locality, etc.	Character.	Soft. °F.	Flow. °F.	Water.	1. Inor-ganic.	1. For or-ganic.	1. Bitu-men.	2. Inor-ganic.	2. For or-ganic.	2. Bitu-men.	3. For or-ganic.	3. Bitu-men.	Remarks.
4706	Station 1, lake...	Porous	200	210	29.97	25.67	7.78	36.58	36.66	11.11	52.23	......	......	On road at southwest corner.
4707	2, streets.	"	180	200	30.13	25.55	8.21	36.11	36.57	11.75	51.68	......	......	100 feet on.
4708	3, north..	"	180	200	29.76	25.79	7.29	37.16	36.72	10.38	52.90	......	......	200 feet on.
4709	4.........	"	180	200	28.67	26.38	7.64	37.31	36.98	10.71	52.31	......	......	300 feet on.
4710	5.........	"	180	200	28.34	26.20	7.41	38.05	36.56	10.34	53.10	......	......	400 feet on.
4711	6.........	"	190	200	28.39	26.31	7.35	37.95	36.74	10.26	53.00	......	......	500 feet on.
4712	7.........	"	190	200	28.37	26.35	7.21	38.07	36.79	10.06	53.15	......	......	600 feet on at water's edge, bet. islands.
4713	8.........	"	190	200	28.96	26.30	7.14	37.60	37.02	10.05	52.93	......	......	700 feet on.
4714	9.........	"	190	202	28.07	26.41	7.41	28.11	36.71	10.31	52.98	......	......	800 feet on.
4715	10.........	"	184	200	30.05	25.30	7.33	37.32	36.17	10.48	53.35	......	......	900 feet on.
4716	11.........	"	190	210	26.80	26.94	7.48	38.78	36.80	10.22	52.98	......	......	1,000 feet on.
4717	12.........	"	180	200	28.11	26.45	7.43	38.01	36.79	10.34	52.87	......	......	1,100 feet on.
4718	13.........	"	Lost	......	......	......	......	......	......	......	......	......	......	1,200 feet on.
4719	Old soft spot....	Tough	180	190	24.53	26.60	7.57	41.31	35.24	10.03	54.73	......	......	Old soft stuff, 50 feet west of course.
4720	Soft spot........	Soft	170	185	34.10	25.05	6.35	34.59	38.00	9.64	52.36	......	......	Soft spot, collected in cans.
4721	Station 14........	Porous	180	200	25.77	27.17	7.69	39.37	36.60	10.36	53.04	......	......	1,300 feet on.
4722	15.........	Old soft	180	200	25.86	27.19	7.86	39.15	36.67	10.53	52.81	......	......	1,400 feet on.
4723	16.........	Porous	180	200	26.80	26.87	7.58	38.75	36.70	10.34	52.96	......	......	1,500 feet on.
4724	17.........	"	190	200	27.62	26.14	7.98	38.26	36.11	11.03	52.86	......	......	1,600 feet on.
4725	18.........	"	190	200	26.90	26.82	7.75	38.53	36.69	10.60	52.71	......	......	1,700 feet on.
4725	19.........	"	190	200	26.87	26.62	8.50	38.01	35.41	11.62	51.97	......	......	1,800 feet on.
4726	20.........	"	200	210	25.78	27.30	8.26	38.66	36.78	11.13	53.09	......	......	1,900 feet on.

TABLE I (CONTINUED). LAKE PITCH.

Serial No.	Locality, etc.	Character.	Soft. °F.	Flow. °F.	Water.	1.			2.			3.		Remarks.
						Inorganic.	For organic.	Bitumen.	Inorganic.	For organic.	Bitumen.	For organic.	Bitumen.	
4727	Station 21........	..	190	210	28.09	25.52	8.06	37.33	36.89	11.21	52.90	......	......	2,000 feet on.
4728	22........	..	230	240	29.94	25.79	7.74	36.53	36.81	11.05	52.14	......	......	2,100 feet on in worked portion.
4729	23........	Traveled	210	220	27.41	26.16	8.05	38.38	36.04	11.09	52.87	......	......	2,200 feet on in worked portion.
4730	24........	Weathered	210	220	29.95	25.51	7.74	36.80	36.41	11.05	52.54	......	......	2,300 feet on at outer edge of road.
4731	25........	..	210	220	30.65	25.66	7.44	36.25	37.00	10.72	52.28	......	......	2,400 feet on at tent, in grass. 2,500 feet.
4732	27........	Grassy	210	220	27.87	26.10	7.66	38.37	36.18	10.62	53.20	......	......	On road Station 25 bears N. 7° E., and old road to Point Boyer N. 57° E.
4733	28........	Traveled	200	210	26.72	26.58	7.30	39.40	36.27	9.96	53.77	......	......	300 feet on.
4734	29........	Porous	190	200	26.43	26.81	7.50	39.26	36.44	10.19	53.37	......	......	600 feet on.
4735	30........	Old soft	180	200	25.96	26.86	7.51	39.67	36.28	10.14	53.58	......	......	900 feet on in old soft stuff.
4736	31........	Near soft	180	200	25.11	27.19	7.87	39.83	36.31	10.51	53.18	......	......	1,200 feet on at the side of soft stuff.
4737	32........	Old soft	180	200	26.49	26.75	7.60	39.16	36.39	10.34	53.27	......	......	1,500 feet on in old soft stuff.
4738	33........	Porous	190	200	26.25	26.84	7.86	39.05	36.39	10.66	52.95	......	......	1,800 feet on.
4739	34........	..	190	220	27.99	26.30	7.99	37.72	36.52	11.09	52.39	......	......	2,100 feet on.
4740	35........	Grassy	210	225	26.12	27.05	7.95	38.88	36.62	10.75	52.63	......	......	2,300 feet on and 150 feet to road.
	Average ...	....	......	......	27.85	......	......	......	36.56	10.57	52.87	16.66	83.34	

TABLE I (CONCLUDED). LAND PITCH.

Locality, etc.	Serial No.	Character.	Soft. °F.	Flow. °F.	Water.	1. Inorganic.	1. For organic.	1. Bitumen.	2. Inorganic.	2. For organic.	2. Bitumen.	3. For organic.	3. Bitumen.
Hadley's, N. of No. 76 Lot C. Crown Land, 1000 ft. from lake bet. it and ravine. — Shipping heap..	4802	Cheese	200	210	27.93	26.80	7.48	37.79	37.19	10.38	52.43	16.52	83.48
Porous lot......	4861	"	200	220	27.53	26.50	7.32	38.65	36.57	10.10	53.33	15.92	84.08
Iron pitch......	4741	"	280	300	0.36	43.41	7.69	48.54	43.57	7.72	48.71	11.91	88.09
" "	4865	"	260	270	0.21	40.96	7.56	45.27	47.06	7.57	45.37	14.30	85.70
Sylvestre's, N. at fork of road, 2,500 feet from lake, on disputed claim. — From excavation	4743	Cheese	270	295	1.64	40.36	7.38	50.62	41.03	7.50	57.47	12.72	87.28
Dos Santos, for Rel-biero, Rudin & Co. on crown land N. of A. King's, 2,900 feet from lake. — From excavation	4748	Cheese	250	280	13.86	33.47	8.02	44.65	38.86	9.31	57.83	15.23	84.77
" "	4866	"	240	262	23.29	29.23	7.40	40.08	38.10	9.65	52.25	15.59	84.41
From shipping heap.	4746	"	260	284	26.34	27.54	8.71	37.41	37.39	11.82	50.79	17.28	82.72
" "	4862	"	210	232	28.91	27.11	7.86	36.18	38.13	10.97	50.90	17.73	82.27
Periera's, Lot 22, S. of Mon Repos on road. — From excavation	4798	Cheese	280	304	24.53	28.98	9.36	37.53	37.88	12.39	49.73	19.95	80.05
" "	4744	"	200	220	29.69	26.41	8.08	35.82	37.56	11.49	59.95	18.40	81.60
Heap on burial ground.	4801	"	200	210	24.65	27.42	7.41	40.52	36.39	9.83	53.78	15.54	84.46
" "	4860	"	210	230	27.61	27.89	7.38	37.12	38.52	10.19	51.29	16.57	83.43
Mon Repos, de Silva, etc. Land in litigation, November, 1891 — Mon Repos......	4803	Cheese	310	328	24.75	35.90	6.44	32.91	47.71	8.55	43.74	16.35	83.65
Opposite lot 8 ...	4805	"	299	320	30.27	26.56	7.61	35.56	38.10	10.92	50.98	17.14	82.36
Turnbull, Stewart & Company's collections from village lots. — From shipping heaps.	4807	Cheese	240	264	23.58	39.09	8.60	37.73	39.37	11.25	49.36	18.55	81.45
" "	863	"	220	240	31.33	26.28	7.51	34.88	38.27	10.94	59.79	17.72	82.28
Village lots. — Benicourt	4804	Cheese	290	318	0.35	39.34	8.82	57.54	39.46	8.85	57.69	14.62	85.38
Lot 56	4799	"	280	300	31.76	25.12	7.54	55.58	36.81	11.05	52.14	17.49	82.51

preparations of the samples. Nevertheless, the closeness of the percentage composition of the original samples is remarkable, and it is plainly no matter of accident. From a mineralogical point of view the water, organic matter not bitumen, and mineral matter must be as much original and essential constituents of the pitch as the bitumen, and must have been derived from the same original source.

TABLE II.

	Average.	Highest.	Lowest.
Water	27.85	30.65	25.77
Inorganic	26.38	....	....
Organic, not bitumen	7.63	....	....
Bitumen	38.14	....	....
When calculated to dry substance:			
Inorganic	36.56	37.02	36.27
Organic, not bitumen	10.57	11.75	9.96
Bitumen	52.87	53.77	51.68

When the analyses of the specimens are calculated to a basis of dry substances, the variations in composition become naturally even smaller and the more striking the uniformity of the proportion of each constituent in the pitch from all parts of the lake.

THE SOFT PITCH.

The soft pitch which is found in the center is, however, in addition to differences in its physical nature, somewhat different in its composition from the pitch of the rest of the lake.

If it is heated for some time there is a great frothing, and an evolution of gas occurs, accompanying the volatilization of the water, together with some of the light oil which it contains. The resulting product is no longer a mass easily kneaded, but resembles more closely an ordinary soft, refined pitch or hard cement. A comparison of the soft material with the average lake pitch is seen in the following figures:

	Soft.	Average lake.
Water and gas	34.10	27.35
Inorganic matter	25.05	26.38
Organic matter not bitumen	6.35	7.63
Bitumen	34.50	38.14
	100.00	100.00

In its natural condition the soft stuff contains more water than the average lake pitch.

When calculated to dry substance the figures become:

	Soft.	Average lake.
Inorganic matter	38.00	36.56
Organic matter not bitumen	9.64	10.57
Bitumen	52.36	52.87
	100.00	100.00

When calculated to inorganic free substance:

Organic, not bitumen	15.55	16.66
Bitumen	84.45	83.34

The substances—

Soften at	170^C	190^C
Flow	185^C	200^C
Volatilize in 10 hours at 400° F	12.24	3.66

The amount of inorganic or mineral matter is somewhat higher in the soft than in the average lake pitch, and the organic matter not bitumen a little lower, but the general relation of the constituents is such as to show them to be of the same origin, the one having merely more oil and being more readily melted than the other, the cause of which will be examined later. It is evident, however, as heat reduces it so quickly to a comparatively solid state, that its softness is somewhat due to its physical condition and the active state of change it is in, as well as to its lower melting point.

LAND PITCH ANALYSES.

An examination of the analyses of the land pitch specimens shows in comparison with those of the lake pitch an apparently very wide variation in composition. Without drawing an average from such a heterogeneous set of specimens the extremes for each determination were found to be:

	Highest.	Lowest.
Water	31.76	0.21

Dry substance:

Inorganic matter	47.71	36.39
Organic matter not bitumen	12.39	7.50
Bitumen	53.78	43.74

While some of the specimens of land pitch contain as much or more water than those from the lake, many, especially the iron pitches, contain much less, a drying out having accompanied the changes in its nature. In the commercial supply, however, which has been sorted and which contains only cheese pitch,

there is probably but a small difference, the average found in the heaps collected for shipment being 27.36 per cent.

In the same way with the other constituents there is a great deal more variation in the samples of land pitch than in those from the lake, and in the iron pitches there is a decided reduction in the amount of the organic matter not bitumen, from that found in any lake specimen; but if we select and average only the analyses of specimens of the commercial supply of land pitch from the heaps, no such striking difference will be found, following being the average and extremes for eight specimens of material ready for shipment:

	Average.	Highest.	Lowest.
Water	27.36	31.33	23.58
Dry substance:			
Inorganic matter	37.74	39.37	36.39
Organic matter not bitumen	10.68	11.82	9.83
Bitumen	51.58	53.78	49.36

There is but little difference from the variation of lake pitch, a point which I demonstrated in 1890.

It is apparent, therefore, that in the commercial supply of land pitch which has been carefully selected and from which alteration products and soil have been excluded there is no essential difference in the relative proportions of mineral matter, bitumen, and organic matter not bitumen from those in the lake pitch. The difference between the two pitches depends, therefore, on some variation in the character of their constituents. The mineral matter and the organic matter not bitumen do not change so as to affect the properties of the pitch, as will be seen when they are described further on. The bitumen in the two pitches must therefore be to some extent unlike, and it is a fact that the original bitumen of the lake pitch has become to a greater or less degree modified in the land deposits. As the soft spots in the lake gradually harden and become like the rest of the surface, so this process continues, making the outer portions of the lake harder than the center and the land deposits harder than any part of the lake. We find evidences of this in the heaps of pitch ready for shipment on the shore. Those of lake pitch rapidly run together and become a homogeneous mass in a short time, while the land pitch, even under the strong tropical sun, still shows the

distinct lumps of which it was originally made up, for a longer
or shorter time, depending on the quality of the land deposit.
With the poorest deposits they remain so loose and friable that
it is possible to shovel over such heaps even after weeks.

The softening and flowing points of the specimens examined
reveal the difference, and the results show the greater softness of
the lake pitch, and were it not for the difficulty of getting rid of
the water in such small samples as were collected of the crude
pitch without losing some of the lighter oils upon which the
flowing point much depends, the relative differences shown in
the tables would be greater and more distinctive.

In consequence of this difficulty of removing the water on a
small scale from specimens, without decided changes in their
character, the comparative study of the bitumen in the two kinds
of pitch has been continued with typical specimens of refined pitch
carefully handled on a large scale.

VARIOUS FORMS OF PITCH NOT OF COMMERCIAL VALUE.

In addition to the forms of lake and land pitch, which are
in use in pavement, there are several forms which have been
mentioned which are of interest as showing the results of age
and the consequent alterations upon pitch. They include the
chocolate-colored alteration products on the exposed surfaces of
land pitch, the friable soil which results from the disintegration of
the oxidized and rotten stuff, and the resonant material existing in
the reefs and shore deposits.

Analyses of these varieties of pitch gave the following results :

No.	Form.	Original substance.				Dry substance.		
		Water.	Organic.	Organic not bituminous.	Bituminous.	Inorganic.	Organic not bituminous.	Bituminous.
4750	Iron pitch, selected ..	9.78	34.13	8.40	47.69	37.83	9.31	52.86
4751	Chocolate, blended ..	3.70	37.90	8.61	49.79	39.35	8.94	51.71
....	Chocolate ...	1.14	36.87	8.38	53.61	37.30	8.47	54.23
4742	Sylvestre soil	35.13	38.47	18.17	8.23	59.30	8.01	12.69
4752	Dundonald soil	7.04	80.17	11.60	1.19	86.24	12.48	12.80
....	Black ledge.	2.27	60.24	14.54	22.95	61.64	14.88	23.48
....	Gray ledge..	1.59	64.73	19.52	14.16	65.77	19.83	14.40

The change that takes place seems, as far as the amount of soluble bitumen is concerned, to be at first very slight, except in color, and then a gradual conversion of the bitumen into organic matter not bituminous, followed by a removal of this organic matter by oxidation. It is a change which is of interest from a technical point of view as illustrating in the strongest way the fact that the difference between land pitch and lake pitch is but the beginning of this process, and that the land pitch is inevitably inferior to that of the lake by just the amount the former has suffered during the process of oxidation, which in some specimens is very small and in others large, depending upon the conditions which have existed under different surroundings.

THE DIFFERENCES IN THE CONSTITUENTS OF LAKE AND LAND PITCH.

Refining pitch commercially consists in heating large quantities in stills or boilers to as high a temperature as will drive off the water in the material and melt it without volatilizing the oils to any noticeable degree, the heat being applied not directly from a fire underneath the vessel, but by conducting the products of combustion around it, beginning at the upper portion of the still. The melted product from which the water has evaporated, the coarser mineral matter subsided, and the lighter organic matter skimmed, is drawn off and is known as refined asphalt, or in Trinidad as epuré. It gives us the bitumen of the pitch in a more available form for investigation, and where the process has been carefully conducted, in one representing very closely its nature and character as found in the original pitch.

SOFTENING POINT.

As has been said, the differences in the pitch from the lake and from the land deposits are first revealed by the lower softening point of the former. In commercial refined asphalt this difference is readily recognizable. Determinations accumulated during the past three years with different cargoes have furnished the following extremes:

	Soft. ° F.	Flow. ° F.
Refined lake asphalt	180–192	189–210
Refined land asphalt	190–237	210–255

From a commercial point of view it is not quite possible to tell from the softening point alone the origin of refined asphalt, where refining has been carefully conducted. The figures, however, are representative of characteristics which can be made visible by reducing portions of the refined asphalt to an impalpable powder when cold, and then allowing them to stand in a small heap at ordinary temperatures, 70° to 80°. Under these circumstances the lake material will become caked and tough after twenty-four hours so that the powdery mass can only be separated with the use of some strength. The best land asphalt adheres somewhat, while the poorer qualities remain in their original powdery condition and in no wise agglomerated.

If, in addition, these preparations are subjected to a temperature approaching or equalling their softening points they will flow if placed on an incline, and the distance covered may be expressed in percentages of some standard sample, thus giving another expression of the quality of the material.

The softening point of refined asphalts is, of course, modified by the care exercised in refining, and somewhat by the portion of the still from which the sample is drawn when any sedimentation has been allowed or excessive heat applied.

Refined lake asphalt of good quality always softens below 190° F., refined land above that temperature.

DISTILLATE AT 400° F.

If refined asphalts of both lake and land origin are subjected for a certain length of time (conventionally ten hours) to a temperature of 400° F. in a well protected retort, the percentage of oil volatilized will be found to correspond to the nature of the bitumen and the source of the asphalt.

Asphalt collected at intervals across the lake and from several land deposits have yielded the following results:

Lake series:

Margin	2.56
Near center	6.18
Center	6.80
300 feet north	4.44
200 feet further	4.28
400 feet further	3.01
100 feet from digging	3.28

Land deposits:
 Point d'Or 1.37
 Bellevue.................................. 1.39
 Brighton 1.32
 Shore 1.20
 Benicourt 0.86

These determinations made by Mr. Bowen on the crude material show what a decided difference there is between pitch from the two sources and that in the lake itself; .the nearer the source is to the center, the larger in amount and the more readily volatile is the oil there present. In the soft pitch there is as much as twelve per cent. of oil which goes over at 400° F., and in the pitch of the semi-soft spots as much as eight.

These results with the crude pitch are quite similar to those obtained with refined material except that as the latter has lost some of its oil in refining they are relatively lower. Good refined lake asphalt will volatilize not less than three per cent. of oil in ten hours at 400°, while land asphalt will rarely equal this and often in the poorer kinds goes below one per cent., while from the hard reefs nothing is volatilized.

The amount of this readily volatile matter is therefore plainly an additional index of the quality of the pitch and its value for paving.

PETROLENE OR BITUMEN SOLUBLE IN PETROLEUM NAPHTHA.

As is well known, all the bitumen of Trinidad pitch is soluble in carbon disulfid, but only a portion of this, which has been called petrolene, is soluble in petroleum naphtha. Determinations made with various refined asphalts show that the percentage of the entire amount of bitumen thus soluble is another index of its quality in the same way as the softening point and the amount of oil volatile. This is naturally so since the softening point is dependent on the amount of oil or pretrolene present, and the matter volatilized is that portion of the same substance which volatilizes at comparatively low temperatures. The following determinations illustrate the variations in refined asphalts from several sources in this respect.

LAKE REFINED, SOLUBLE IN PETROLEUM NAPHTHA.

	Proportion of	
	Entire material.	Bitumen.
Soft, refined	48.36	92.32
Lake, 5306	40.01	70.03
	39.56	69.56
	39.41	69.30
5316	39.50	69.00
5333	41.59	72.37
5330 ..:	41.43	73.60
Old, refined	36.00	66.13
" "	38.14	68.53
Still No. 1, June, 1892:		
First run	38.65	69.97
Second run	37.40	68.48
Third run	37.38	69.35
Still No. 4, August, 1892:		
First run	40.00	69.75
Second run	39.13	69.07
Third run	40.52	72.82

LAND REFINED, SOLUBLE IN PETROLEUM NAPHTHA.

	Proportion of	
	Entire material.	Bitumen.
Soil	5.94	46.82
Chocolate pitch	25.17	48.90
Iron pitch	31.60	64.60
Teneriffe	33.89	64.08
Saracas	35.62	64.53
Jones Point	34.73	59.61
New York	30.31	57.59
No. 1	36.47	65.68
No. 2	37.56	67.37
No. 4	35.14	63.53
No. 7	35.22	65.52
No. 5	34.98	68.27

It is apparent that there is a distinctive difference in the character of the bitumens in the pitch from the two sources, and one which is of value as a means of distinguishing them.

Upon the presence of this oily or soluble bitumen the viscosity and cementitious value of the pitch largely depends, but at the same time it is found that adding asphalt oil to pitch in which it is deficient does not restore or renew the properties which have

been lost. This shows that the absence of the oily bitumen is indicative of changes which have gone on in the whole of the bituminous constituents of the pitch and rendered it harder and more brittle. It is well known that no addition of petroleum or asphalt oil will give to iron pitch any cementitious value, and in the same way it is found that cement made for paving purposes from pitch in which the original oil has suffered change or is lacking wants toughness and tenacity and will not pull out into a long thread, as will that made from lake pitch.

The process of hardening of the pitch seems, therefore, to be connected with a change in this oily bitumen, the more volatile and soluble constituent known as petrolene. The more of this there is present the softer and tougher is the pitch, and as a chemical change goes on and converts it into a harder and less soluble and volatile material, the less yielding and the more brittle the pitch becomes, as is found to be the case in land and iron pitch, which contain the least of it. The soft pitch at the center of the lake was found to volatilize as much as twelve per cent. of oil at a temperature of even 300° F., and in a like way to contain the largest amount of petrolene, or portion of its bituminous constituents soluble in petroleum naphtha.

In the various qualities of Trinidad pitch it will be found, therefore, that the proportion soluble in petroleum of the entire bitumen varies from ninety-two to fifty-seven per cent. and that the more life the pitch has the larger is the percentage.

In other asphalts the same distinction between the bituminous constituents is found; and in the case of a maltha from California, where 99.9 per cent. of the bitumen is of a nature soluble in petroleum, the pitch is liquid, while a Venezuelan sample, where 68.49 per cent. out of a total bituminous content of ninety-seven per cent. is soluble, compares in consistency with lake pitch, the percentage of the whole bituminous matter which is soluble in petroleum naphtha in the two pitches being: Venezuelan, 70.5 per cent.; lake, seventy per cent.—a form of statement in which the inorganic matter of the Trinidad pitch has no influence. A more extended examination of the relations of the two classes of bitumen is now in progress.

SPECIFIC GRAVITY.

Determinations of the specific gravity of refined asphalts in the solid state are readily made, and have been found characteristic of the source of the material, that of the lake pitch being lower than that from the land deposits.

Following are accumulated results, which show the relation of water and pitch at 77° F., 25° C., which has been found to be a more suitable standard in our climate for normal temperature than the usual 60° F.

SPECIFIC GRAVITY OF REFINED PITCH.

Lake :

3213, June, 1890	1.3666
4719, old soft spot	1.3581
Pocahontas, 1890	1.3708
5316, August, 1892, Barber Asphalt Paving Company	1.3751
5306, April, 1892, Barber Asphalt Paving Company	1.3800
5299, August, 1892, Barber Asphalt Paving Company	1.3898
4559, Denver	1.3866
Spring, 1892, Barber Asphalt Paving Company	1.3861
5333	1.3771
5330	1.3857

Land :

3533, 1890	1.4916
4750, iron pitch	1.4506
Baltimore, 1890	1.4339
Cranford Paving Company, 1890	1.4329
4802	1.4216
2853, Teneriffe	1.4081
Jones Point, 1892	1.4002
5274	1.4013
5312	1.3930
4560	1.4067
4801	1.3950
5328	1.3969
5329	1.3988
5331	1.4187
5334	1.4232
5332	1.4316

The specific gravity of refined pitch is naturally largely influenced by the amount of mineral matter which it contains, and it seems to be a fact that refined land pitch usually contains the

more mineral matter, due to greater sedimentation being possible with the lake material, which has greater fluidity on melting.

In well-refined land pitch, in which the amount of mineral matter is at times no greater than that in good refined lake asphalt, there is still found, however, a sufficient difference in specific gravity to allow a ready distinction between the two. This shows that there must be a decided difference in the specific gravity of the bitumen in the two pitches, and points to the conclusion that the bituminous material soluble in petroleum naphtha, in undergoing the chemical change which makes it insoluble, less volatile, and more brittle, increases at the same time in density.

Actual determinations of the specific gravity of the soft bitumen soluble in petroleum naphtha and of the hard bitumen soluble only in carbon disulfid show that that of the latter is sufficiently higher to produce a decided effect on the specific gravity of the refined pitch when the relative proportions are varied, petrolene or soft bitiumen having a specific gravity of 1.032 and asphaltene or hard bitumen of 1.142.

It therefore happens that the pitch from the soft spot has the lowest specific gravity, while that of iron pitch is the highest.

There can, of course, be cases where confusion might arise from over heating lake pitch in refining, or by the unknown addition of oil after refining to land pitch. In the former case the asphalt would, even as from a lake source, be of little value and could properly be classed with land pitch, and in the latter case the fraud would be detected by other means, and as the production of refined asphalt and asphaltic cement should be watched and inspected through all the steps of preparation, any such injury or falsification would of course be discovered.

In the table it will be seen that, although there are considerable variations in each class, depending on the care in refining and in collecting the pitch, the specific gravity of refined lake asphalt has not been found to go above 1.3900, nor that of refined land asphalt to fall below that figure.

In this characteristic we have one of the quickest means of distinguishing between refined asphalts, and with the use of all the determinations which have been mentioned I have never been deceived as to the origin of any specimen of refined material,

although the eye and a knife blade are perhaps sufficient for a skillful person.

VALUE OF CERTAIN CHARACTERISTICS OF REFINED ASPHALT AS A MEANS OF IDENTIFYING ITS SOURCE.

As an illustration of how the determination of the characteristics which have just been described is of value as a means of identifying the source of asphalt, the following case, where seven samples of refined were submitted to me with no further identification than being numbered, will serve. An examination gave the following results, according to which they were classified correctly, as was afterwards shown :

EXAMINATION OF REFINED ASPHALTS.
(Origin unknown to the analyst.)

Chemist's no.	5328	5329	5330	5331	5332	5333	5334
Capt. Fiebiger's no.	1	2	3	4	5	6	7
Specific gravity $\frac{77°}{77}$F..........	1.3969	1.3988	1.3857	1.4187	1.4316	1.3771	1.4232
Softens	195°	197°	190°	195°	198°	183°	210°
Flows	208°	215°	205°	210°	210°	198°	230°
Bitumen..........	55.52	55.75	56.29	55.31	51.22	57.47	53.75
Organic matter not bituminous.	8.96	8.06	8.05	7.84	7.78	7.05	8.01
Inorganic matter	35.52	36.19	35.66	36.85	41.00	35.48	38.24
Bitumen soluble in petroleum naphtha	36.47	36.79	41.43	35.14	34.98	41.59	35.22
Per cent. of total bitumen soluble	65.68	65.99	73.60	63.53	68.27	72.37	65.52
Viscosity	Semi-adhesive	Semi-adhesive	Adhesive	Friable	Very friable	Adhesive	Friable
Quality	Best land	Best land	Average lake	Average land	Poor land	Best lake	Average land
Source as eventually revealed ..	Saracas Jones Pt.	Saracas Jones Pt.	Lake B. A. P. Co.	Barbadian Jones Pt.	Barbadian Jones Pt.	Lake B. A. P. Co.	Miscel. Jones Pt.

It seems, therefore, that there is such a decided difference in the nature of the bitumen found in the different deposits at La Brea that they can be distinguished without difficulty, and that in consequence it is only rational to suppose that the freshest and least altered deposits must be the most valuable.

THE NATURE AND ORIGIN OF THE TRINIDAD PITCH DEPOSITS.

To obtain a better understanding of the nature of Trinidad pitch deposits and of their origin, a more extended examination has been made of some of the constituents than has so far been mentioned. As has been said, the great uniformity of the relations between the water, mineral matter, bitumen, and organic matter in all the unaltered pitch, shows that their formation must have been simultaneous and that none of them can be considered as adventitious. It would be impossible for water in any adventitious way to become so intimately mixed with the bitumen as to form practically an emulsion. In refining, much of this water rises and floats upon the surface of the pitch and can be collected, of course, somewhat changed by evaporation and oxidation. After many attempts to separate it in other ways without success, it has been examined in this form, and its nature is probably quite as well shown. It is of a distinct saline and thermal character, containing a large amount of salts in solution, which explains the efflorescence seen upon the crude pitch and which were for a long time attributed to sea salt.

The results of an analysis were as follows:

ANALYSIS OF ASPHALT WATER.

Specific gravity 1.017 $\frac{15^\circ \text{ C.}}{15^\circ \text{ C.}}$ Reaction strongly acid.

In one kilogram.

Cl	6.7757	NH$_4$	0.4071
SO$_3$	5.5409	K	0.3391
SO$_2$	0.0467	Li	0.0271
S$_2$O$_7$	Traces	Ca	0.5280
H$_2$S	Trace	Mg	0.2666
S	Trace	Fe	0.0720
SiO$_2$	0.0688	Al	Trace
B$_2$O$_3$	0.0117	Mn	None
I	0.0008	Cs and Rb	None
Br	Trace	Organic	0.4901
P$_2$O$_5$	None.	Oxygen	......
Na	6.5149		
			21.0896

The presence of borates, iodids, so many forms of sulfur compounds, and other characteristics show at once that this water

must be of the same origin as that of many thermal springs; that is to say, volcanic. The steam which is formed in the refining of the crude pitch at first contains much hydrogen sulfid, which blackens all the white-lead paint in the vicinity of the refinery. This, under favorable conditions of heat and evaporation, at times changes to sulfurous anhydrid, which again bleaches out the white paint, and the condensed steam shows a strongly acid reaction. In the presence of one another the hydrocarbons and the thermal water at high temperature evidently produce complicated reactions.

The principal salts in solution are, in the order of their amount, sodic chlorid and sulfate, ammonic, potassic, and ferrous sulfates; borates, iodids, etc., being present in smaller amounts, the aggreegate being so large as to make it an unusually strong mineral water.

MINERAL MATTER.

The inorganic or mineral matter which is left in burning off the hydrocarbons and other organic substances is an ash, flesh colored from the iron oxid derived from the ferrous sulfate of the. water in the pitch.

It consists of the salts dissolved in the water and of some clay mixed with a large proportion of silica in the form of minute sharp conchoidal fragments of quartz. An analysis showed:

	Per cent.
Silica, clay, etc., insoluble in acid	82.63
Soluble salts, alumina and iron, etc.	17.37
	100.00

Of the insoluble portion nearly ninety-five per cent. is silica. Under the microscope this silica is very sharp, with a conchoidal fracture and largely in a very impalpable state of division. Its origin in this fine condition is obscure. The entire absence of lime, except the very small proportion in solution in the waters, is also a remarkable feature of the ash. Carbonates would, of course, not be expected, but other lime salts might well be.

ORGANIC MATTER NOT BITUMEN.

The organic matter not bituminous possesses no distinctive characteristics. A small portion of it is, no doubt, derived from grass, stems, sticks, etc., blown on the lake, a little more organic

matter of this nature being found in the pitch on the margins of the lake than in that toward the center ; while the soft pitch contains nearly one per cent. less than the average lake deposit. The largest part of it, however, is an impalpable powder without any signs of organization, and is apparently a by-product in the formation of the bitumen.

BITUMEN.

The bitumen of Trinidad asphalt, like that of many others, is of two kinds. One is soluble in petroleum naphtha, while the other is only soluble in carbon disulfid. The former is a brownish, sticky material, which at summer temperatures can be drawn out in strings. The latter is a brittle, glassy, black pitch, readily reduced to powder and not melting on the application of heat. The names which Boussingault gave years ago to the substances which he incompletely separated from asphalt will serve well to distinguish them, namely, petrolene for the bitumen soluble in petroleum, and asphaltene for that only soluble in carbon disulfid.

To the petrolene the Trinidad pitch owes its cementitious value, and the larger the proportion the better the pitch, as has been already shown. The nearer the center of the lake pitch is taken, the more petrolene it contains.

Asphaltene seems to be an alteration product of petrolene. It has a higher specific gravity than petrolene, 1.142 as compared to 1.032, a difference which, as has been shown, enables us to distinguish the quality of refined pitches to a certain extent by their specific gravity.

Petrolene consists of a series of hydrocarbons of varying consistency from a light oil of specific gravity below 0.9 to those heavier than water. These hydrocarbons include several series, both saturated and unsaturated.

A more extended examination of them is in progress and will be published in the future.

THEORIES OF THE FORMATION OF BITUMEN.

Several theories have been advanced, some of which attribute the formation of the pitch to chemical causes and the others to animal or to vegetable remains. From either of these sources it may have reached its present position through springs or distil-

lation, or have been deposited in place with the rocks in connection with which it is found. The character of bitumens from different localities is very variable, and they are without doubt not all of the same origin or chemical nature.

Suggesting the chemical origin of some forms of bitumen, Berthelot, in 1869, advanced a theory based on the action of carbonic acid on the alkaline metals at high temperatures, but this has not grown in favor.

In 1877, Mendeléeff, from a study of the oil wells of the Caucasus and elsewhere, concluded that the origin of bitumen could not be in organic remains, as this would presuppose the formation of so much carbon in geological times, when none was known to exist. He therefore proposed that with the admission of the existence of carbids of metals at high temperatures deep down in the earth, the origin of bitumen could be attributed to the infiltration of water, and its action on the carbids with the formation of saturated hydrocarbons and metallic oxids, the former being transported to the surface by aqueous vapor, where they might appear in springs or as impregnating rocks.

This explanation of the origin of petroleum finds support from the following facts: The predominance at the surface of the earth of elements having a small atomic weight; the appearance of petroleum in directions corresponding to great circles; the relations remarked by several naturalists, particularly M. Abech, between petroleum and volcanic manifestations.

The fact that the pitch deposits of Trinidad lie directly on the line of the strong volcanic action which appears in the lesser Antilles, and contain such a distinctive volcanic water as a prominent constituent would seem to confirm the application of Mendeléeff's theory to at least this particular case, especially as he suggests that saline waters accompanying bitumens might prove on investigation to support his views.

On the other hand, Wall and Sawkins, who looked very carefully into the origin of the deposits from a geological point of view, but without any chemical investigations of the composition of the crude pitch, advance the theory of origin in vegetable remains. On pages 1 and 3 of their report they say: "A sectional exposure at Point d'Or is extremely instructive. The

asphaltic shale is perceived over a bed of loose, yellowish sand, free from bitumen. The asphaltic shale is brown, porous, shaly sand, including masses of asphalt rather irregularly distributed, but with manifest tendency to stratification. Porosity is due to loss of material, evidently asphaltic, which has run and secreted itself in lines of weakness. The expansive force so exerted has elevated laminæ 30° to 50°. When this bituminous bed thins out, asphalt disappears, as in Point d'Or pasture."

This seems to them to justify the conclusion that the "origin of the asphalt is in the bed and is not ascending, as some evidence of passage would appear. The same conclusions are drawn from repeated strata from Point La Brea to Guapo." They conclude that the asphaltic beds were originally carbonaceous or lignitic shales and discovered what they considered to be conversion in every stage from organic texture to obliteration of the wood. They found no pitch in strata of pure carbonaceous content, but that it is characteristic of those with much earthy matter and is a modification of the production of lignite.

In Wall and Sawkins' day but little excavation had been done for pitch, and those made since in large numbers have afforded a much better opportunity for studying the origin of the land deposits.

They do not confirm their observations. On the contrary, the deposits show no signs of conversion of vegetable matter into bitumen, and that their origin has been largely a mere infiltration of the soil by the bitumen as already formed, and which has subsequently changed in its chemical nature under the conditions there existing. A large proportion of the bitumen has undoubtedly come from the lake and another portion has been forced up from below in a quite liquid state in much the same way as is seen at the soft spot in the lake.

I do not believe, therefore, that the " bituminous substances at La Brea, whether liquid or solid, have been formed from vegetable material by direct conversion at ordinary temperatures."

No evidence of this appears in the material which is ejected at the soft spot, which is in an active state of chemical change, and like all other data, gives a far more reasonable basis for the assumption of volcanic origin.

THE COMMERCIAL HISTORY OF THE PITCH INDUSTRY.

Sir Walter Raleigh is said to have pitched his ships with the bitumen of La Brea as long ago as the days when he sailed the Spanish Main, but the lake remained nothing more than a natural wonder, practically until the seventies. In 1851 the Earl of Dundonald leased a large part of it for twenty years and also some of the adjoining land. In 1856 a joint stock company was organized, called the Trinidad Petroleum Company, Limited, for the purpose of making oil from the pitch or from an oil spring near at hand. To this company the Dundonald lease was assigned. Remnants of their works are to be seen to-day at the oil spring, a short distance below the lake on the shore. Their attempts were failures, and the company went into liquidation in 1866. Mr. T. A. Finlayson was its Trinidad manager, and apparently succeeded to its right under the leases, as he continued to ship pitch, without doubt, from the lake. Most of such shipments were for use in mastic, and were largely sent to France and Germany. In 1858 Wall and Sawkins say that pitch for export was all obtained at La Brea point, and from 1862 to 1866 O'Connor Brothers shipped from the same place.

All attempts to make the pitch of commercial importance had failed up to 1871. In that year we find the New York and Trinidad Asphalt Company bringing pitch in some amount to New York. Hitherto endeavors had been made to imitate the asphalt-rock pavements of the continent with mixtures of coal tar and sand only, but many of these proving great failures, Mr. E. J. De Smedt, formerly of this office, experimented with Trinidad asphalt, and in 1870 laid a crude pavement of this material in Newark. In 1871 or 1872 he also laid another piece around Battery Park, New York, and in 1873 or 1874, one on Fifth Avenue, in front of the Worth monument, which, with one or two resurfacings remained until 1886. In 1874 or 1875, Eighteenth street was paved with a Trinidad composition between Fourth avenue and Irving Place ; Twenty-eighth street, between Broadway and Fifth avenue; and Thirty-eighth street, from Fifth Avenue to Madison avenue. These surfaces were laid on old stone pavements as a base, and the one on Twenty-eighth street is still in use, although it has been much patched ; Eighteenth street

was resurfaced eight or ten years ago, and Thirty-eighth street in 1891.

These experiments attracted considerable attention, and when Congress, in 1875–76, provided for paving Pennsylvania avenue from the Capitol to the Treasury, the commision appointed to select the best form of pavement, Gen. Wright, Gen. Gilmore, and Architect Clark, decided to put down an asphalt pavement; and from the Capitol to Sixth street to lay compressed rock asphalt, and the remainder Trinidad sheet asphalt. The contractors for the work were the New York and Grahamite Company, of which George Averill was the manager, and with whom De Smedt was connected.

The rock-asphalt surface was soon condemned for the slipperiness which is always characteristic of this pavement, and no more has since been laid. The Trinidad surface was so satisfactory that when the permanent Board of Commissioners of the District of Columbia came into power in 1878 they decided to confine the pavement of streets not of excessive grade or having heavy or confined traffic to Trinidad asphalt.

CONCLUSIONS IN REGARD TO THE PRESENT POSITION OF THE PITCH INDUSTRY, AND THE RELATIVE VALUE OF LAKE AND LAND PITCH.

In the light of the foregoing investigations and facts the following brief conclusions appear to me to be justified in regard to the present status of the pitch industry :

Land pitch is inferior to lake pitch in cementitious value. Land pitch is better in quality the nearer its source is to the lake. Land pitch can readily be distinguished from lake pitch by certain characteristic differences when examined in the refined state.

Lake pitch is superior for paving purposes because it contains more bitumen in a viscous or cementitious form, and less of the brittle bitumen, which is of smaller value.

The addition of oils to the latter form of bitumen will not produce as desirable cement as that made from the lake asphalt. It will not draw out to a long string like lake asphalt cement, but breaks short and is of the same comparative value that cold short is to tough and good iron.

Land pitch requires the addition of more petroleum oil to produce a cement of required consistency than lake pitch.

Land pitch would never be used were lake pitch generally available.

The poorer forms of land pitch are now generally conceded to be unfit for paving ; and the question may therefore be asked where the line or degree is to be drawn as to what is suitable.

The large extent of the lake deposit permits of an unfailing and uniform supply which can always be depended on and always handled in the same way.

Various deposits of land pitch vary widely and demand great skill and manipulation to produce even the best results attainable with this kind of pitch, although the care used in selection and cutlassing has improved the character of the shipments decidedly.

This element of manipulative skill in handling the materials properly for the production of a good pavement, that is to say a thorough understanding of the technique of the industry, in the works and in the street, should without doubt have equal consideration with the quality of the materials in use.

A skilled laborer can probably make a better pavement from land pitch than an unskilled one with lake pitch.

With the enormous growth of the industry within a short period of time the demand for experts has continually exceeded the supply. Everyone engaged, from the superintendents and foremen down to the laborers, has a decided influence on the character of the finished work. Those who refine and handle the crude asphalt, who make the asphaltic cement and compound the surface mixture, and those who rake and roll the material in the street, according to the degree of their knowledge, experience, and skill, contribute to the success or failure of the work. The older paving companies certainly control the best labor and brains, having had the longest and most successful experience, and the city of Washington as a pioneer in laying asphalt surfaces has probably at present as able a set of men employed by its contractors as can be found. The character of our street surfaces of all ages attests this fact, and it would seem to me to be undesirable at the height of our success to enter into any experiments with new and untried conditions and materials.

Should any competitors of the present contractors or methods desire to exhibit their work there is no reason why they should not be given an opportunity to prove it of superior character by laying a certain amount at their own expense where it would be subjected to fair conditions of traffic and wear in comparison with our own asphalt surfaces.

I should, therefore, in the light of all my experience and knowledge, unless further evidence is adduced or great pecuniary advantages offered, reccommend that the District of Columbia provide in its specifications that lake pitch be used in pavements for which it contracts, and that the work shall be done by the most skillful and experienced labor and in the most approved manner.

ПORE ABOUT SPELLING.
BY EDWARD HART.

In a review of the report of the Committee on Spelling and Pronunciation of the American Association for the Advancement of Science, contained in the *American Chemical Journal* for January, Dr. Ira Remsen writes as follows, quoting from an article by the writer in the September, 1892, number of this Journal:

"'These proposed changes were carefully canvassed with those gentlemen who have made the English language their life-study and who were unanimous in favor of them. They were made the subject of a number of reports to the American Association for the Advancement of Science and were favored by a large majority of those present. In drawing up the report the committee sought and obtained the opinions of a number of chemists not members of the Association, and so far as it was possible to obtain an expression of opinion the recommendations voice the wish of American chemists.'

"In the article from which this quotation is taken occurs the passage, 'Man is a conservative animal and does things in a certain way because he is accustomed so to do them. This conservatism increases with age until it becomes almost impossible to shake it off.' In the face of these fundamental truths one hesitates to express an opinion on the recommendations of the American Association, fearing that to differ may be to proclaim one's self an ass, and the ass is even more conservative than man."

These quotations taken alone totally misrepresent the spirit of the article which contained only a fair and accurate statement of the case. The statements quoted are true and can be verified.

That the philologists are in favor of shortening and simplifying English spelling is well known, and the philologists, as the best judges, were consulted constantly as the work went on. The Committee did consult all the American chemists whose names were known to it and several letters were sought and received, among others, from Dr. Remsen himself. The last statement quoted meets his views evidently, since it is spoken of with the others as "fundamental truths"—which seems more emphatic than necessary, though otherwise unobjectionable. Dr. Remsen goes on to say:

"This spelling, as every one knows, is a hard subject to deal with, and the Committee of the American Association deserves much credit for the care they have given to their work. Their recommendations seem on the whole to be wise, and it would perhaps be well if every chemist adopt them. There is one chemist known to the present writer who is willing to acknowledge that he doesn't like 'sulfur,' but he is also willing to acknowledge that this is no argument against it."

Exactly so! And the present writer is also willing to acknowledge that he did not like "sulfur" at first. Even so good a thing as a bath is disagreeable until what the small boy calls the "misery" of the first plunge is over.

A story comes from Washington anent this very word. A certain government official in addressing a learned association meeting there said that he had that morning declined to approve a report laid before him, for the reason that it contained the word "sulfur" spelled without the ph, which it should have by right of its Greek origin. "He did not know," said my informant, "that the word came from the Latin and never should have been spelled with the ph."

PATENTS OF INTEREST TO CHEMISTS.
EDITED BY A. H. WELLES.

Horace F. Brown has three patents, two on an ore roasting furnace (489,142–143) and one on a condensing furnace for lead fumes (489,144). William H. Howard invents an apparatus for removing matte from slags (489,307), and Walter E. Koch has patented a new furnace for heating steel ingots (489,017). 490,451 is a method for making metal plates by John B. Nau, and 490,236

a process for manufacturing sheet iron by Walter D. Wood. John B. Jenkins heats malleable cast iron, cast steel, Bessemer steel, etc., in contact with a compound consisting of granulated or powdered charcoal, manganese dioxid, chlorid of sodium, cyanid of potassium, and chlorid of ammonium, as a new process for the manufacture of steel (490,660). Another process (491,035), Taylor Allderdice, inventor, consists in placing a sufficient quantity of free carbon in a ladle to raise the carbon content of the steel to the point desired, and then pouring the metal into the ladle from the converter.

Frederick P. Dewey treats mixtures conlaining sulfids of silver and copper with concentrated sulfuric acid, then adds water, precipitates the silver by copper, and recovers the sulfate of copper from the remaining solution (490,068). William B. Jackson patents his process for treating ores (490,659), the steps in which are first chlorination of the ores, then solution of the chlorids in hyposulfite, and finally precipitation of the metals by the action of one or more zinc plates.

To obtain gold, silver, and copper from their ores, Andrew French (490,193) mixes the pulverized ores with small percentages of niter cake or sodium bisulfate and common salt, treats in a furnace at a red heat, then leaches the mass. Prof. William H. Greene and Dr. Wahl have received a patent (490,961) for their process for producing metallic alloys. In brief, a metallic oxid is heated with a silicid of a metal capable of uniting with the reduced metal, in a furnace in the presence of suitable fluxes. Prof. Green and Dr. Wahl also have a patent process for manufacturing manganese and its alloys, free from carbon (489,303). The ore is digested with dilute sulfuric acid, then the manganese in solution is reduced first to manganous oxid, then to the metallic state by heating in a furnace free from carbon, in contact with the chemically equivalent quantity of a metal capable of removing its oxygen.

Frank M. Harris amalgamates a metal, and unites the amalgam to an "amalgamable metallic base" and by expelling the mercury thus unites the two metals (489,077). 489,632 applies to regenerating or cleaning electrolytic solutions by freeing from arsenic by mixing them with metastannic acid, heating until

a combination is effected between the arsenic and metastannic acid, and the salt formed is precipitated.   The metastannic acid is then recovered (489,633) by dissolving the compound in concentrated hot sulfuric acid, adding an oxidizing agent, and then diluting the mixture until free metastannic acid is precipitated.

A metallic alloy, consisting of pig iron, ferro-manganese, chromium, tungsten, aluminum, nickel, copper, and bar iron, is claimed by Frederick W. Martino (489,314) for the manufacture of tools and other purposes, and Frank G. Stark (490,174) makes an alloy consisting of fifty-six parts copper, forty parts zinc, two parts iron, and one part aluminum.   In connection with aluminum, we may mention a composition for soldering the metal which Georg Wegner proposes (490,840), viz.: 165 parts lead, 100 parts tin, and nine parts zinc, and his process for electroplating aluminum (490,841), which is as follows: The metal is first dipped into a bath at boiling temperature containing cyanids of silver and mercury to heighten its activity, then electrically coated with zinc, in a bath containing chlorid of zinc and sulfate of soda, to protect the aluminum against the acid bath in coppering, silvering, gilding, etc.   Andrew Honman and Victor Vulliez, of Victoria, protect their process, in this country, for the manufacture of white lead by U. S. patent 489,254.   The reduced galena is roasted, treated with neutral lead acetate, the basic lead acetate formed is conveyed to a settling tank, then discharged into a closed vat and the solution is subjected to the action of carbonic acid to precipitate the white lead.

Camille L. C. Bertou proposes (489,624) a process for precipitating oxid of tin from solutions, which consists in precipitating the tin from solutions containing it by carbonate of lime, adding the precipitant while the solution is exposed to the air at a temperature just below boiling, then cooling the liquid after complete precipitation, washing the precipitate with cold water and then suspending it in a solution of an alkaline carbonate, the strength of which is gradually increased until it has a faintly alkaline reaction.   489,460–461 are two patents granted to Parker C. Choate, for a process for obtaining metallic zinc.   An ore of zinc carrying lead is heated with a reducing agent in a furnace, to which air is admitted, so as to volatilize the lead and zinc and

other volatile constituents, heating the mixed lead and zinc fumes to "volatilize those constituents more volatile than zinc, and to granulate and condense the mass." The zinc is then reduced with carbon and distilled and the molten lead is drawn off. Robert F. Nenninger produces zinc oxid from the sulfate or sulfite of zinc (489,873) by precipitating the solutions with lime, boiling the collected precipitate with a concentrated solution of zinc sulfate, and after filtering the solution, the filtrate is evaporated to dryness and leached with water.

Numbers 489,574-575-576 and 881 are patents for obtaining and separating sulfid of nickel granted to Robert M. Thompson. The crude nickel obtained by smelting the ore with a suitable flux is resmelted with niter or salt cake with an excess of carbon, the sodium sulfid formed uniting with the nickel to form nickel sulfid, which is separated by specific gravity. John L. Thomson (489,882) uses instead of niter or salt cake in presence of carbon, sulfids of any of the alkaline metals or ammonium to produce sulfid of nickel. Arthur S. Grant, *et. al.* (490,847) fuses ores containing nickel with calcium sulfate or other sulfates and the less easily oxidizable metals, as nickel, are left as sulfids. C. J. Theuerner (490,816) subjects silver coated with oxid to an electrolytic bath containing prussiate and cyanid of potash, the oxid-coated silver being suspended as the anode, for the purpose of cleaning the silver.

[The specification and drawing of any U. S. Patent in print may be obtained from the publisher of this Journal. Applications must be accompanied in all cases by twenty-five cents for each patent specification wanted. BE CAREFUL TO WRITE THE NUMBER LEGIBLY.]

NEW BOOKS.

LABORATORY CALCULATIONS AND SPECIFIC GRAVITY TABLES. BY JOHN S. ADRIANCE. 2nd edition, revised and enlarged. New York: John Wiley & Sons. 12mo., 114 pp. Interleaved.

The calculations are based on Professor Clarke's 1882 table of atomic weights, and "have been made with the greatest care, so that they may be thoroughly depended on in every particular."

The tables given comprise Absorption of Carbonic Acid in HCl; Absorption of Nitrogen in Hypochlorite Solution; Alcohol

Table; Alloys and Coins; Atomic Weights; Atmosphere, N,
and CO,, weight of one cc.; Barometer and Beaumé Tables;
Thermometer Tables; Nitrogen to Ammonia, etc.; Conversion
Tables; Directions for making Reagents; Mercury, Volume and
Density; Molecular Weights; Percentage Composition; Specific
Gravity of Acetic Acid, Alcohol, of Aluminum, Ammonium,
Barium, Calcium, Cobalt, Copper, Iron, Lead, Magnesium,
Potassium, Sodium, Tin, and Zinc Salts; Specific Gravity of
Acids; Saccharometer Tables, etc., etc.

The book is well gotten up and seems to be free from the pad-
ding which is too common in books of this class.

THE COAL-TAR COLORS, WITH ESPECIAL REFERENCE TO THEIR INJURI-
OUS QUALITIES AND THE RESTRICTION OF THEIR USE. A SANITARY and
MEDICO-LEGAL INVESTIGATION. BY THEODORE WEYL, WITH A PREFACE
BY PROFESSOR SELL. Translated with permission of the author by
Henry Leffmann, M. D., Ph.D. Philadelphia: P. Blakiston, Son & Co.
12mo., 154 pp. Price, $1.50.

The coal-tar preparations, in the form of dyes, and more
recently as medicines, have become so common that some knowl-
edge of their properties becomes indispensable to the physician,
and is not out of place with the chemist. Dr. Weyl has tried, as
he says in the preface, not to be "too medical for the chemist,
nor too chemical for the physician."

Only a part (those commonly used) of the many known colors
have been examined. Most of the experiments were made on
dogs. The colors tested comprise some members of each of the
following groups: nitroso colors, nitro colors, azo colors, and
diazo colors. The book also contains a summary of the laws
in force relating to the use of these colors in Germany, England,
France, Italy, and Austria-Hungary. The book is well trans-
lated, and is a good specimen of the printers' art.

CHEMISTS' POCKET BOOK OF READY REFERENCE. BY BREYER AND
SCHWEITZER, Analytical and Consulting Chemists, 159 Front Street,
New York. Price, $1.00. Published by the Authors, 1893.

An effort to make the chemist's work easier is always praise-
worthy, and the compilation of Breyer and Schweitzer is intended
to bring near the day when chemical operations will be con-
ducted on a nickel-in-the-slot principle. All the information

which is necessary for chemical operations is to be found, or is supposed to be found, within the limits of the book. The chemists preparing this book have, according to their modest introduction, had "an extended experience in the largest chemical establishments of the world, and in the most renowned laboratories for research." This has been supplemented by the "knowledge gained as consulting chemists to the leading manufacturers of the United States." All this accumulation of research and experience has been expended in "selecting only such matter as may have value to our esteemed readers."

The authors acknowledge their indebtedness to "standard books" for a great many of the tables offered, but they desire to "call attention to the fact that a great number of others are the result of our own investigations." The experience which the authors have had, as noticed from the introduction, was provided at Badische Anilin und Soda-Fabrik, at Ludwigshafen on the Rhine, the Strontianite Sugar Refining Company, at Dessau in Anhalt, F. O. Matthiessen & Wiechers, Jersey City, N. J., the American Zylonite Company, Zylonite, Mass., while their didactic experience was gained as assistant professors at the Agricultural Experiment Stations of Munster and Westphalia, and in the Agricultural High School of Berlin, and in the organic laboratory of the University of Heidelberg.

The book opens with calendar notes for 1893. There is no originality displayed in the arrangement of the days of the year. They follow each other in regular order, and hence it is supposed that this calendar is not one of the results of the authors' investigations.

The two most important items connected with each month are the statements of the periods at which the sun rises and sets. There is no item of information more important in a chemist's life than the hour of sunrise. The eagerness which every chemist displays to be at his desk and engaged in chemical manipulations, before the sun is fully up, meets in this way a sympathetic response.

Under the head of "Information for the Laboratory" is given a series of tables taken almost bodily from the "Chemiker-Kalender." The authors have taken the trouble to translate the

names of the chemical substances but have omitted to translate the symbols, as is indicated on page five, where hydriodic acid and iodin are written JH and J,, respectively.

Of the purely chemical tables, sixty-nine are taken from the "Chemiker-Kalender" and, with two exceptions, in the exact order in which they occur in that compendium. One or two remarkable variations from the order of the arrangement in the "Chemiker-Kalender" are noticed in the book, but without any sufficient reason. For instance, after copying some of the tables on page.49 of the Kalender, the authors rush *per saltum* to page 308 for the purpose of copying the table on the strength of the solutions of bleaching powder; after which they placidly "return to their muttons" and continue seriatim to page 64, when another break is made to page 305, after which page 65 is returned to, then the selections continued in regular order.

In the specific gravity of solid and liquid elements on page 6 the specific gravity for bismuth, which occurs twice in the table of the original, is only given once, namely, for the quickly cooled; while the specific gravity for that which is slowly cooled is more than two points higher, being 9.94 instead of 7.68. In the same table the specific gravity for gold is only given for the cast gold and not for the hammered or pressed gold which is the one in ordinary use. The authors have also omitted the range of specific gravities in steel which is given in the original table from 7.62 to 7.81, giving only the lower number 7.62.

In the table for specific gravities of various solid substances, the one item of gunpowder is represented in the original table of the "Chemiker-Kalender" as having the apparent specific gravity determined in three conditions: first, loosely poured, second, shaken, third, stamped. In the table as given no distinction is observed but the astounding statement is made that the specific gravity of gunpowder varies from 0.836 to 1.745.

These serve as illustrations of the slovenly way in which the tables from the "Chemiker-Kalender" have been translated.

The amount of labor necessary to translate the Arabic numerals is certainly enormous and these have been pretty well transferred, but when it comes to the other part of the work much carelessness seems to have been permitted. This is particularly noticed in

the fidelity with which the errors of the original tables are copied. It may be said that to copy an error is the sincerest form of plagiarism and the authors of the work have evidently earned the gratitude of the compilers of the "Chemiker-Kalender" for the sincerity which they have manifested in faithfully portraying even the weaknesses of the original. One dangerous instance of this is noticed in the transcription of Rossetti's table for density and volume of water on page 7, taken from page 26 of the Kalender. Owing to a typographical error in the original, the figures for the volume of at temperatures above 30° are wrong. In illustration of this attention is called to the fact that a barbarous system of printing the original has been followed, in which, instead of giving the whole number, it is left to the reader to deduce it from the numbers preceding. The original table has fallen into the error of misplacing the numbers in the table, almost uniformly, by one decimal point; in fact, all the numbers from 40° to 90° are erroneous. These errors have been faithfully copied in the transcript. When it is remembered that the table for the density of water is one which the chemist has frequent cause to refer to the repetition of such an error becomes the more reprehensible. The original table of Rossetti was published in Pogg. Ann., Vol. 5, page 268, 1871. .The actual figures taken from the original table for the volume of water at 40° are 1.00770 ; taken from the table in the "Chemiker-Kalender" they are 1.004770 ; taken from the actual figures given in the Breyer and Schweitzer pocket book they are 1.004770. All the following numbers are erroneous except the one for 100°.

It is difficult to see the principle which has guided the distinguished authors in making their selections from the "Chemiker-Kalender." For instance, page 58 of the Kalender contains five tables giving the specific gravities of solutions of ferric sulfate, potash and ammonium alum, potash alum, chrome alum, neutral potash tartrate and soda potash tartrate. The authors have selected out of the lot the table of specific gravities of potash alum, chrome alum, neutral potassium tartrate, and sodium potassium tartrate. So far as practical use is concerned, the tables which are omitted might just as well have been included, as they are just as valuable practically as the others for chemists. In

general, the same remarks may be applied to the tables omitted from the "Chemiker-Kalender."

Under the head of sugar, on page 68, the saccharometer of Soleil-Ventzke is referred to. It is stated that in order to find the amount of sugar in 100 cc. of a solution the number of degrees found by direct polarization is to be multiplied by 0.26048 grams. The question might arise in arithmetic what the product would be when degrees are multiplied by grams? According to the statement made, it gives the amount of sugar. This new rule in arithmetic then reads: Degrees multiplied by grams gives amounts.

It is stated that as the specific rotatory power of cane sugar increases between ordinary limits with a decrease of the concentration, a correction of $-0.1°$ is to be used for readings between $17°$ and $84°$. The amateur polarizer is left with this lucid explanation for his guidance in the manipulation of the instrument.

The table which immediately follows gives a comparison of the saccharometer degrees with the degrees of Beaumé's areometer. No statement whatever is made of the temperature at which this comparison is made, although the percentage of cane sugar is given for each degree of the scale. No distinction is made between the use of the term saccharometer as applied to a polarizing instrument and "saccharometer" as applied to a density instrument.

The value of a table depends upon its accuracy and the ease of the method of applying it. The amount of invert sugar which is represented by the amount of copper reduced is a variable which changes with every change in the percentage of invert sugar in the solution and with the amount of copper present. It is not seen how any worker with invert sugar would understand without very careful and elaborate study what is meant by the table 86, and it is therefore of questionable usefulness.

The above illustrations have been mentioned, not for the purpose of carping criticism, but to call attention to the fact that even those who esteem it their especial duty to give instruction to American chemists, in regard to the proper methods of analysis, may themselves not be altogether free from criticism, even in almost bodily transferring a worthy foreign publication to the American printing press.

JournalofAnalytical&AppliedChemistry.

XXV. A NEW EXTRACTION APPARATUS.

BY H. W. WILEY.

THE desirability of having an extraction apparatus for use with ether and alcohol in which there are no cork or other stoppers, has long been realized. This led to the construction of the apparatus of Knorr, in which there was only one joint, and this was made by sealing with mercury. This apparatus of Knorr has been used in the Chemical Laboratory of the Department of Agriculture for nearly three years and with perfect success. The only objection which can be urged against it is its cost, the glass blowing being expensive.

To secure, if possible, a small and inexpensive apparatus, I made some experiments with some of the metallic condensers which have already been in use. The metal condensers are usually of two forms; one being in the form of a copper ball, the interior of which is kept filled with cold water, and the other a series of double conical copper condensers exposing as large an amount of surface as possible to the ether and alcohol vapors.

The form of condenser finally adopted is shown in Fig. 1, in which the tube E serves to introduce the cold water to the bottom of the condensing surface. The tube D serves for conveying away the waste water. The tube F serves for the introduction of the solvent by means of a small funnel. When the solvent is introduced and has boiled for a short time, the tube F should be

closed.   In each of the double conical sections of the condenser a circular disk B is found, which causes the water flowing from A upward to pass against the metallic surfaces of the condenser.

A section of the double conical condenser is shown in Fig. 2. It is provided with two small hooks *hh*, soldered on the lower surface, by means of which the crucible C can be hung with a platinum wire.   The condenser is best made smooth and circular in form.
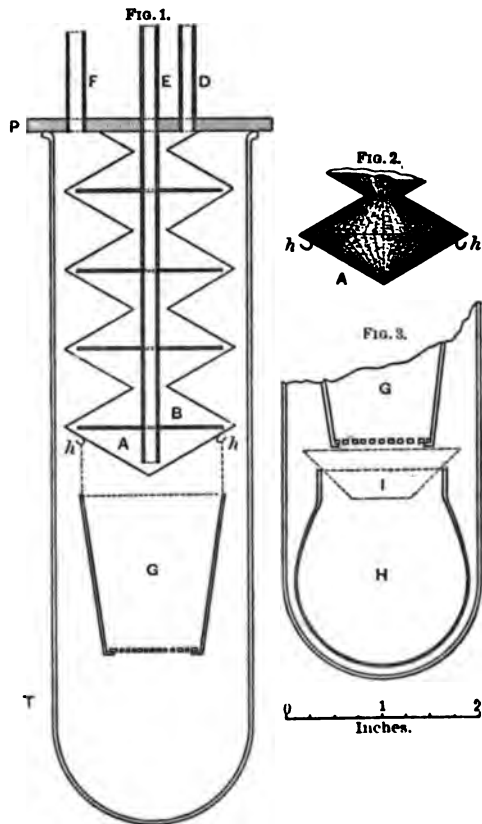
The crucible G, which holds the material to be extracted, can be made of platinum, but for sake of economy I have had them made of porcelain.   The bottom of the crucible is left open excepting a small shelf as indicated, which supports a perforated disk of platinum on which an asbestos film is placed.

The whole apparatus is of such size as to be easily contained in the large test-tube T.

Fig. 1.

Fig. 2.

Fig. 3.

Inches.

The mouth of the test-tube is ground so as to fit as smoothly as possible to the turned brass plate of the metallic condenser P.

In case it is desired to weigh the extract it may be done directly by weighing it in the test tube T after drying in the usual way at the end of the extraction; or a glass flask H, made to fit freely into the test tube, may be used, in which case a little mercury is poured into the bottom of the tube to seal the space be-

tween H and T. To prevent spirting of the substance in H, projecting any of the extracted material without or against the bottom of the crucible G, the funnel represented by the dotted lines in Fig. 3 may be used.

This apparatus is extremely simple, inexpensive and effective. It permits in every case, if desired, a double weighing both of the residue and of the extracted matter. It saves much time in weighing in case the extraction with ether is to be followed by extraction with alcohol.

Heat may be applied to the test tube either by hot water, or steam, or, best in our experiments, by an Acme Bunsen burner which permits of the flame being turned down to minimum proportions without danger of burning back. When the test tube alone is used it is advisable to first put into it some fragments of pumice stone, particles of platinum foil, or a spoonful of shot, to prevent bumping of the liquid when the lamp is used as the source of heat.

Any air which the apparatus contains is pushed out through F when the boiling begins, the tube F not being closed until the vapor of the liquid has reached its maximum height. With cold water in the condenser the vapor of ether very rarely reaches above the lower compartment and the vapor of alcohol rarely above the second.

When the plate P is accurately turned so as to fit the ground surface of the mouth of T, it is found that ten cc. of anhydrous ether or alcohol are sufficient to make a complete extraction, and there is scarcely any loss of solvent in six hours. The thickness of the asbestos film in G, or its fineness, is so adjusted as to prevent too rapid filtration so that the solvent may just cover the material to be extracted, or, after the material is placed in a crucible, a plug of extracted glass wool may be placed above it for the purpose of distributing the solvent evenly over the surface of the material to be extracted.

This apparatus is not only inexpensive, but simple in its operation, and when the room is not too warm one stream of water will serve to operate half a dozen extractors by connecting one with the other. On account of the simplicity and inexpensiveness of this apparatus it will take the place of the Knorr appa-

ratus, although it is not claimed that it is in any way superior to the Knorr apparatus in efficiency.

The porcelàin crucible G has two small holes drilled into its sides near the top for the purpose of holding the wires which attach it at *hh*. The flask H has a small hole drilled in the neck near the top by means of which it can be lifted out of the test tube with a wire hook.

XXVI. AN IMPROVED METHOD FOR THE GRAVIMETRIC ESTIMATION OF FURFUROLHYDRAZONE.*

BY W. H. KRUG.

In 1873 Dr. Scheibler[1] extracted exhausted sugar beet chips with lime and obtained metapectic acid. On treating this with dilute sulfuric acid a sweet crystalline substance was formed which Scheibler assumed to be a new sugar and called arabinose. For a long time this sugar was considered to be a true glucose, and in 1880 Kiliani[2] stated it to be identical with lactose. Subsequent investigations by Scheibler[3], Claësson[4] and Lippman[5] proved this erroneous, but it was not until 1887 that the true composition of arabinose was discovered. It that year Kiliani[6] ascertained the composition of the lactone of arabinose-carboxylic acid to be $C_6H_{10}O_6$. He therefore reasoned that arabinose could not contain more than five carbon atoms and this was borne out by an analysis of the phenylosazone of arabinose which he found to be $C_{17}H_{20}O_4N_4$.

This discovery was of the greatest interest as arabinose was the first member of the group $C_5H_{10}O_5$ so far observed. Another pentose had been prepared but its true nature had not been recognized. In 1886 Koch[7] treated wood gum with dilute sulfuric acid and obtained a sugar which he called xylose. Later he prepared this sugar from various woods, jute, and straw. When the true composition of arabinose was discovered, attention was naturally directed to xylose which had been similarly prepared, and in 1889 Tollens[8], by applying Raoult's method of estimating molecular weights, found both arabinose and xylose to be $C_5H_{10}O_5$.

*Presented to Washington Chemical Society, Feb. 9, 1893.

Arabinose has been prepared from gum arabic[9], cherry gum[10], gum tragacanth[11] and wheat bran, while only lately Stone[12] extracted large quantities of xylose from corn cobs. The outer seed coats of barley yield both arabinose and xylose.

Arabinose crystallizes in prisms, $(a)_D = 104.4$ to 105.4, melting point $160°$. Xylose also crystallizes in prisms $(a)_D = +20°$ to $21°$, immediately after solution $(a)_D = 38.8°$, melting point $145°$.

Both pentoses reduce Fehling solution and are dextrorotatory. They differ from the glucoses, however, in that they are not fermentable and produce large quantities of furfurol when distilled with dilute acids. They do not occur ready formed in nature but are the hydrolysis-product of certain plant constituents which are collectively called pentosans. The nature of those pentosans is at present not well understood. They are generally spoken of as gums, and are extracted from cellular tissues of plants by weak alkali. They have been variously designated as metapectic acid, arabin, wood, gum, and so on. Wherever they occur they may be detected by their yielding furfurol when distilled with a dilute acid. The first action of the acid is to break up the pentosan molecule into a pentose. If this process is hydrolytic, as it is now generally accepted to be, the reaction will be
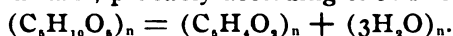
$$(C_5H_8O_4)_n + (H_2O)_n = (C_5H_{10}O_5)_n$$
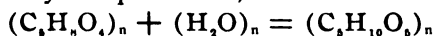
and the resulting pentose will weigh more than the pentosan. The next action of the acid then is to break up the pentose molecule forming furfurol, probably according to this reaction

$$(C_5H_{10}O_5)_n = (C_5H_4O_2)_n + (3H_2O)_n.$$

Small quantities of furfurol may be detected by placing a drop of the distillate on filter paper moistened with anilin acetate. One part of furfurol in 100,000 of water will give a brilliant red color with this reagent.

A large number of substances has been examined in this manner and the pentosans have been found to be very widely distributed. This immediately establishes the importance of estimating them as they are among the constituents of feeding stuffs and have a certain food value. Their discovery in this connection and accurate determination is only one step toward clearing away the conventional term "nonnitrogenous extract." This term has, so far, been used to designate a large number of

food constituents which include the sugars, starches, gums, pectins, and so on. The true carbohydrates, *viz.*, the sugars and starches, we have heretofore estimated by converting into glucose, but even this involves grave errors, as the first action of the inverting acid would be to change the pentosans present into pentoses, and these reduce Fehling solution and are thus always calculated as glucose. Stone[13] found that in solutions of one per cent. or less, one mg. arabinose precipitated 1.9 to two mg. Cu, while under the same conditions 1 mg. xylose precipitated 1.86 to 1.959 mg. Cu. They have therefore a higher reducing power than dextrose, which is the most strongly reducing glucose. The following table from Tollens, Handbuch der Kohlenhydrate, p. 284 will illustrate this even better. The reduction is stated in mg. sugar required in one per cent. of solution to entirely precipitate the copper from one cc. Fehling solution.

Arabinose	0.004523
Xylose	0.004617
Dextrose	0.004753
Levulose	0.005144
Invert sugar	0.004941
Galactose	0.005110
Milk sugar	0.006757
Maltose	0.007780

This shows arabinose to be the strongest reducing sugar yet studied, with xylose closely following it.

Stone found that the pentosans resisted digestion to a remarkable degree, manure from cattle fed on maize ensilage yielding 2.88 per cent. furfuramid and from cattle fed on dried corn fodder 3.94 per cent. furfuramid. Thus the importance of determining them and their food value is quite apparent. We will take, for instance, the case of brewers' grains. We wish to determine their food value, that is the extent to which the carbohydrates have been removed by malting and fermentation. The usual method is to treat with acid to invert the starch and estimate the resulting glucose by Fehling solution. Here, however, the pentosans enter as an unknown factor. The treatment with acid will convert them into pentaglucoses capable of reducing as much Fehling solution as ten per cent. of glucose, and by calculating this reduction as starch we commit a grave error both by ascrib-

ing a food value to an almost indigestible constituent and by considering the malting and fermentation as less perfect than it might be. Starch may in such a case be practically absent. All past work on feeding stuffs, with regard to the carbohydrates present and the corresponding food value, seems to be misleading, the pentoses corresponding to most of the reactions of the true carbohydrates while differing in their physiological value. Fortunately, both have a most characteristic reaction which has been made the basis of several methods of estimating them. This reaction is the formation of furfurol by the action of dilute acids. Furfurol was first obtained by Dobereiner[14] by distilling wheat bran with strong sulfuric acid and manganese dioxid.

Stenhouse[15] found that it was not necessary to use the latter, and by using equal parts of bran, acid, and water obtained a larger yield of furfurol, and Fownes[16] by using half as much acid and water increased the yield still more. Babo[17] obtained furfurol by distilling bran with zinc chlorid. In the improved method twenty-five per cent. acid is used and the crude furfurol obtained amounts to about three per cent. of the weight of the bran used. The distillation is carried on until three-fourths of the liquid has passed over and the furfurol is purified by fractional distillation.

The increase in yield occasioned by diluting the acid, shows the greatest danger in this method, namely, the destruction of the furfurol formed by using too strong an acid, and early in their investigations on this point Tollens and Allen[18] abandoned sulfuric acid as giving too low results and substituted hydrochloric acid. After an extended series of experiments, Tollens and de Chalmot[19] concluded that hydrochloric acid of 1.06 specific gravity produced the best results. The formation of furfurol and continual removal by distillation has been the first step in all the methods so far proposed for the estimation of pentosans and pentoses, and they only differ in the manner of estimating the furfurol in the distillate. As the process of distillation as proposed by Tollens and de Chalmot is so far the best I will give it in full:

Five gms. of the substance are heated with 100 cc. of hydrochloric acid, specific gravity 1.06, in a flask of from 250 to 300 cc. capacity. The flask is provided with a rubber stopper,

through which passes a separatory funnel and the delivery tube
which connects with a Liebig's condenser.   Tollens recommends
heating in a bath of Rose's metal, but Stone has found that the
distillation can be carried on successfully with a Bunsen burner,
using a wire gauze and regulating the flame so that ten cc. distill
over every five minutes.   The distillate is collected in a gradua-
ted cylinder and as soon as thirty cc. have distilled over, they are
replaced by thirty cc. of acid of the same strength, run in drop
by drop from the separatory funnel.   This is continued until the
distillate shows no more furfurol on placing a drop on filter paper
moistened with anilin acetate, which is usually the case in about
two hours, when from 300 to 350 cc. of distillate have been
obtained.   I have found in most cases, however, that the last
trace of the furfurol was not removed until 375 or 400 cc. were
distilled over, and it is therefore imperative that the last dis-
tillates be tested before the operation is interrupted.

The first method proposed for the determination of the furfurol
in the distillate depends upon the reaction between ammonia and
furfurol, furfuramid being precipitated[20], $(C_5H_4O)_3N_2$.   This
method is extremely tedious as it involves the concentration of
the furfurol solution by fractional distillation after neutralizing
the hydrochloric acid present with sodium carbonate.   Ammonia
will not produce a precipitate in anything less than a saturated
solution of furfurol and as the furfuramid is quite soluble, the
method fails to give results which even approach the entire
amount of furfurol present.   Although this method was used in
a number of researches on pentosans and pentoses it was only on
account of the absence of a better method.   It has now been
totally abandoned.

The methods now in use depend upon a reaction which is
common to ketones and aldehydes, namely the precipitation of a
hydrazone by means of phenylhydrazin.   Furfurol is very sensi-
tive towards this reagent.

$$C_6H_5NHNH_2 + C_5H_4O_2 = C_6H_5NHNC_5H_4O + H_2O$$
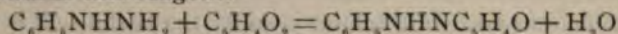
The first method using this reaction was a volumetric one,
and was devised by Tollens and Günther[21].   The distillation is
carried out as described above.   The distillate is collected in
in a large beaker, neutralized with sodium carbonate, and acidi-

fied with acetic acid. Phenylhydrazin solution of known strength is then run in drop by drop until a drop of the liquid will not redden filter paper moistened with anilin acetate. The reaction is complete when no coloration appears after ten hours have elapsed. The phenylhydrazin solution is prepared by dissolving five gms. of pure phenylhydrazin and three gms. of glacial acetic acid in distilled water and diluting to 100 cc. It must be only slightly opaque and must be renewed after twenty-four hours. At the same time 0.2 to 0.3 gm. furfurol is carefully weighed, diluted to 500 cc., titrated as above, and the value of the phenlhydrazin thus determined. The operation is carried on at room temperature and the amount of furfurol found is calculated to arabinose or xylose by means of factors which have been determined by ascertaining the amount of furfurol obtained from the pure pentoses. Tollens found that these varied with the amounts of arabinose or xylose used. Using 0.5 to 1 gm. of arabinose he obtained from fifty-one to fifty-seven per cent. furfurol, using from two to five gms. only from forty-two to fifty per cent. furfurol. In the case of xylose he obtained 53.9 to 55.61 per cent. furfurol for 0.5 to 1 gm., and 50.05 to 50.69 per cent. furfurol for two gms. xylose. The factors are therefore not accurate, and vary with the amount of pentose present.

Later de Chalmot and Tollens[72] used a gravimetric method depending on this reaction, weighing the furfurolhydrazone separated on addition of the phenylhydrazin. The distillation is carried on as in the volumetric method, the distillate being collected in a beaker marked at 500 cc. neutralized with sodium carbonate and acidified with acetic acid. If less than 400 cc. of distillate have been collected, sodium chlorid must be added in such quantity that the neutralized liquid will contain 81.5 gms. This is obtained by adding for every fifty cc. less than 400 cc. 10.2 gms. of sodium chlorid. When this has dissolved the liquid is made up to 500 cc. Ten cc. of a solution of phenylhydrazin acetate is then added, and the liquid stirred continously for half an hour. When this is done the furfurolhydrazone will separate very nicely in the form of small reddish brown crystals. The tolerably clear liquid is then filtered through an asbestos filter such as is used for glucose determinations, using a suction pump

to hasten the operation. The suction must be gradually applied so that the precipitate does not clog. The beaker and precipitate are washed with 100 cc. of water. The precipitate is then dried in an air bath by drawing air previously dried over sulfuric acid through it. The bath is kept at 50° to 60°. The tube is dried for one and one-half hours, weighed, the hydrazone dissolved and washed out by means of alcohol, the tube dried again for thirty minutes and weighed. To obtain the furfurol, the weight of hydrazone is multiplied by 0.516 and 0.025 grams added which represents the average amount of furfurol held in solution as hydrazone by the liquid and wash water. To calculate the pentoses certain factors have been worked out by Tollens which I append at the end of the article.

Less than one per cent. pentose cannot be determined as this corresponds exactly to the amount of furfurol which the liquid and wash water are capable of dissolving.

Before mentioning another method proposed for the determination of furfurol I will describe the modifications I have applied to the above method. After precipitating the hydrazone as directed by Tollens and filtering, I noticed that the filtrate, after standing some time, yielded a second precipitate of furfurolhydrazone. This was also observed by Mr. Maxwell of our laboratory, and I therefore concluded to let the liquid stand over night before filtering. The filtrates from liquids which stood over night invariably remained clear.

The next difficulty which I encountered was in satisfactorily collecting the precipitate after it had formed. A considerable quantity always adhered to the stirring rod and the beaker, and as it was of a tarry nature it could not be removed by any of the usual means. I then decided to avoid this by washing the beaker and the precipitate in the tube with 100 cc. of water to remove all the salt, drying both at a gentle heat, and redissolving what remained in the beaker with alcohol. The alcohol used to dissolve the hydrazone in the beaker was poured on the precipitate in the tube, and I found that I could completely dissolve the precipitate with from thirty to forty cc. of alcohol. The alcoholic solution was collected in a small weighed flask, the alcohol gently evaporated, and the last traces of water removed by heating to 60° and

forcing a current of air into the flask.   In this manner I avoided a very troublesome step in the method which otherwise would have caused a serious error, it being almost impossible to collect all the precipitate.

Stone[23] has proposed a volumetric method for the estimation of the furfurol which depends for an indicator on a reduction of Fehling solution by phenylhydrazin.

A standard solution of phenylhydrazin is prepared by dissolving one gram of the chlorid with three grams of sodium acetate in water and making up to 100 cc.   Such a solution contains 0.747 grams of phenylhydrazin; or, in one cc., 0.001494 grams, which is theoretically equivalent to 0.001328 grams furfurol.   The solution is standardized by titrating against a solution of furfurol of known strength.   This is most conveniently prepared by purifying furfurol by treatment with sulfuric acid and potassium dichromate, and fractional distillation, precipitating with ammonia, re-crystallizing the furfuramid from alcohol, and drying over sulfuric acid. One gram of this furfuramid is dissolved in dilute acetic acid and diluted to one liter, each cc. then containing 0.0010746 grams furfurol.   The phenylhydrazin solution is unstable and must be made fresh every day.

The titration is carried out as follows:

Twenty-five cc. of the distillate are placed in a four ounce Erlenmeyer flask, twenty-five cc. of water added, and a certain quantity of the phenylhydrazin solution run in from a burette. The flask is then heated quickly to the boiling temperature.   If much furfurol is present, the liquid becomes turbid and pale yellow.   As soon as ebullition occurs, the flask is cooled in a stream of cold water, and when thoroughly cool a portion is filtered.   The filtrate should be pale yellow and perfectly clear. If it becomes turbid on standing a few seconds it should be refiltered.   Two cc. of this filtrate are placed in a test tube with four cc. of fresh Fehling solution, shaken, and quickly heated to boiling.   If an excess of phenylhydrazin is present the dark blue color will rapidly change to a greenish yellow.   If too little phenylhydrazin has been added the operation is repeated, using one cc. more, the method being wholly analogous to the old method of titrating invert sugar solutions.

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According to Tollens this method has, however, no advantages over Günther's volumetric method. Both have been practically abandoned in favor of the gravimetric method. This, however, involves such errors due, first, to the possibility of destroying some of the furfurol during the distillation, and, secondly, to the solubility of the furfurolhydrazone in the liquid and wash water, that we must consider the problem of satisfactorily estimating pentoses to be still far from solution, although the modification above described makes the gravimetric method of easy manipulation.

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FACTORS FOR CALCULATING FURFUROL TO PENTOSE (TOLLENS).

Obtained from 5 gms. substance, per cent. furfurol.	Factors for arabinose.
2½ per cent. or less.	$\frac{100}{53}$
5 " " or more.	$\frac{100}{1\,u}$

Per cent. furfurol.	Factors for xylose.
1 per cent.	$\frac{100}{70}$
2½ " "	$\frac{100}{56}$
5 " " or more.	$\frac{100}{51}$

Per cent. furfurol.	Factors for pentaglucoses.
2½ per cent. or less.	$\frac{100}{40}$
5 " " or more.	$\frac{100}{52}$

NOTES ON THE QUALITATIVE EXAMINATION
OF PHENACETIN.

BY CHARLES PLATT, A. C.

Having recently been retained as witness in a Government case involving the identity and purity of a certain drug, phenacetin, it has occurred to me that the scattered literature regarding this new preparation which was collected at that time, and the results of the long series of tests applied, may be of interest to chemists in general. I wish first to acknowledge my indebtedness to *The Pharmaceutical Era, The Druggists' Circular, The Western Druggist, Squibb's Ephemeris, The Analyst, The Journal of the Society of Chemical Industry, The Zeitschrift für Analytische Chemie* (Fresenius), *The Pacific Druggist* and other publications whose files have furnished many of the data which follow.

Phenacetin first made its appearance through the agency of Dr. O. Hinsberg and was brought before the medical world in 1887 by Dr. A. Kast. Though since that time it has become a familiar remedy to the medical fraternity, still the chemistry of its composition and the tests for its identity and purity are little known among chemists. Its medicinal value is as an antipyretic, efficacious in a single large dose rather than in continued smaller ones, producing no nausea or vomiting, followed by no collapse or other deleterious effects common to most of the other preparations. It is non-poisonous even in doses far exceeding the medicinal.

Phenacetin is the acetyl product of para-phenetidin, or in other words, the ethyl ether of the para-amidophenols having the formula $C_6H_4(OC_2H_5)NHC_2H_3O$.   It is a white crystalline powder without taste or odor, melting at about 135° C.   This melting point varies within a few degrees and in several samples examined, which were undoubtedly pure, it stood at 132.5° C. in each

case.   A fall of 2° C. below this would, however, render the purity of the sample a matter of suspicion.   There are four steps involved in the preparation of phenacetin from phenol, which is the starting point in its manufacture, and these, though simple, require care and attention that the resulting drug may be of the requisite purity.   First, the phenol is converted to nitrophenol by gradually adding it (one part) to two parts of nitric acid in four of water.   An oil separates which is washed and distilled with steam, when the volatile ortho-nitrophenol distills over, leaving the non-volatile para-nitrophenol as a residue.

$$C_6H_5OH + HNO_3 = C_6H_4(NO_2)OH + H_2O.$$
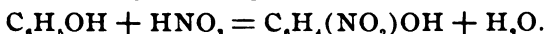
In the second step the ethyl radical, C_2H_5, is substituted in the hydroxyl group of the nitrophenol by treatment with ethyl iodid forming ethylnitrophenol.

$$C_6H_4(NO_2)OH + C_2H_5I = C_6H_4(NO_2)OC_2H_5 + HI.$$
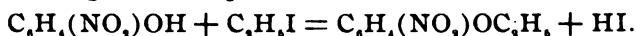
The third step consists in treatment with sodium amalgam, whereby the nitro radical of the ethyl-nitrophenol is reduced to amidogen with the formation of phenetidin.

$$C_6H_4(NO_2)OC_2H_5 + 3H_2 = C_6H_4(NH_2)OC_2H_5 + 2H_2O.$$
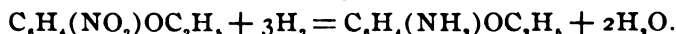
The final step is the treatment of phenetidin with anhydrous acetic acid, thus substituting the radical C_2H_3O for one atom of hydrogen in the amidogen group.

$$\bullet \quad C_6H_4(NH_2)(OC_2H_5) + C_2H_3OOH =$$
$$C_6H_4(OC_2H_5)NHC_2H_3O + H_2O$$
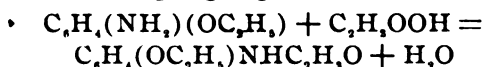
As phenacetin is a bi-derivative of benzene it occurs in the three isomeric forms as ortho, meta, and para-phenacetin, the first with a melting point of 79° C., the second melting at 97° C., and the third at 135° C.   The ortho and the para-phenacetin are both of value physiologically, while the meta-phenacetin is nearly inactive.   The para-phenacetin is that used in medicine and, as mentioned, is white and tasteless, while the ortho-phenacetin which has occasionally been used is grayish and leaves a slight pungent after taste.

The tests for the identity of phenacetin are not conclusive, taken separately, but require careful comparison, and it is only by a number considered collectively that one can arrive at posi-

tive results.   We have first the melting point, the solubilities, and finally the isolated reactions, which fortunately are not difficult to obtain.   For adulteration, the melting point gives the best evidence, though there are a number of tests which will be described later.

Phenacetin melts at about 135° C.; it is but slighly soluble in cold water, though more readily in hot, and is freely soluble in alcohol, acetic acid, sulfuric acid, hydrochloric acid, lactic acid, and in glycerin and chloroform.   The solution in sulfuric acid is colorless when cold, but turns pink when warmed and yellowish-brown when strongly heated, which latter tint it preserves after cooling.   The other solutions named above are colorless and those in water and alcohol are neutral in reaction.

Heated on platinum foil without contact of the flame phenacetin fuses and evaporates leaving no residue.   If ignited, however, it burns with a clear yellow flame leaving a faint brownish coloration on the line of the last contact.

If about 0.1 gm. of phenacetin be boiled in one cc. of hydrochloric acid, and the solution after dilution with water be cooled and filtered from the reprecipitated crystalline mass, the addition of two or three drops of potassium dichromate produces a fine ruby red color.

A similar test is made with bromin water.   A small amount of the phenacetin is dissolved in boiling water, cooled and filtered as before ; bromin water is added until a yellow color is produced, when the solution should remain clear ; a cloudiness would indicate adulteration.

Boiled with hydrochloric acid with the addition of ferric chlorid, phenacetin gives a red color.   This is considered by some one of the best tests for its identity.

Autenrieth and Hinsberg give the following test :   Ten to twelve per cent. nitric acid added to phenacetin in a test tube and then heated to boiling produces the nitro derivative in bright yellow crystals with an orange colored solution above.   As the liquid cools more of the crystals separate out until, if not highly diluted, the entire mass becomes crystalline.   If this is left exposed to the air for several days a slow change takes place, the mass becomes darker and finally nearly black, losing its crystal-

line nature and becoming fluid. The ortho-nitrophenacetin recrystallizes from water in beautiful yellow crystals melting at 103° C. Heating with an alcoholic solution of potash, ortho-nitrophenetidin is formed, crystallizing in long red needles, which when reduced by zinc dust in an alkaline-alcoholic solution yield a white crystalline body, ethoxyphenylenediamine, $C_2H_5OC_6H_4(NH_2)_2$. Ortho-nitrophenetedin recrystallized from alcohol forms fine red prisms melting at 113° C.

If phenacetin be heated with alcohol and sulfuric acid, the characteristic odor of ethyl acetate is observed; by heating the solution thus formed with caustic potash and chloroform, the carbylamin reaction is obtained; by boiling with caustic potash, alcohol is formed. This latter reaction also serves to distinguish the phenacetin from acetanilid.

The tests remaining are concerned chiefly in the examination of phenacetin for impurities and admixtures but, as will be seen, many, if not most, yield color reactions and are admirably adapted for additional proofs of identity. We might separate the two classes of tests but in the limits of the present article we deem it more expedient to give them but once. The impurities likely to be met with in phenacetin are three. First, acetanilid or antifebrin, which being approximately but one fifteenth of the price of phenacetin may have been added to increase the profits. There is more in this than simple fraud upon the buyer as, according to Schroeder, phenacetin when taken internally yields phenetidin and para-amidophenol both harmless bodies, while acetanilid yields anilin.

Acetanilid or phenylacetamid, $C_6H_5NHC_2H_3O$, is prepared by boiling anilin with glacial acetic acid. It forms in crystalline plates, neutral in reaction and odorless, though producing a slight burning sensation when placed on the tongue. It melts at 112° and distills unchanged at 292°. It is difficultly soluble in cold water (1–60) and in hot (1–50), but is more soluble in alcohol, ether, chloroform, and benzol. At 6° C. 189 parts of water dissolve one of acetanilid. With concentrated nitric acid, acetanilid, accord-

ı Reuter speaks of para-phenetidin as poisonous, affecting the kidneys and producing nephtrities, especially in continued small doses. The fact remains, however, that phenacetin is not poisonous even though according to Schroeder, phenetidin is produced in the stomach.

ing to one authority, yields a colorless solution, according to another the solution is first brown, then blue, then colorless (E. Utrecher). The writer found the solution to be colorless when made in the cold, but on the first application of heat it turned to a yellow and then to a dark red, with evolution of fumes of the oxids of nitrogen. It is important to keep this reaction in mind when testing phenacetin by the method of Autenrieth and Hinsberg.

Antipyrin or phenyldimethylpyrazolon, $C_6H_5(CH_3)_2C_3HN_2O$, may also be found with phenacetin. It forms in rhombic prisms and is odorless, possessing a pleasant sweetish-bitter taste. The melting point is 113° C. and decomposition takes place at a higher temperature, though it may be boiled at 141.5° when the pressure is reduced to 265 mm. It is readily soluble in water and alcohol. Heated with nitric acid until the reaction commences, antipyrin produces a purple colored solution. On pouring this into water and filtering, the filtrate shows a purple red color and the precipitate on the paper violet.

Para-phenetidin may be present as an impurity though probably in small quantity and from accident or imperfect manufacture.

As stated above the melting point of the sample is an excellent criterion of its purity, and this is particularly true with acetanilid owing to its low melting point. A mixture of phenacetin with five per cent. of acetanilid shows at 113°–114° C. drops of liquid on the sides of the tube, and the whole mixture melts completely at 127°–128°. The indophenol reaction has been used as a test for acetanilid but the writer has not found it entirely satisfactory. The following tests, though they fail absolutely to distinguish acetanilid in the presence of phenacetin or vice versa, are valuable as means of rapid distinction between the two.

1. One cc. of a solution of phenacetin in concentrated hydrochloric acid, well cooled, gives with chlorin water a red coloration, while acetanilid under the same treatment produces a dark blue color which afterwards fades.

2. The corresponding tests may be obtained by substitution of bleaching powder solution for the chlorin above.

3. One cc. of the hydrochloric solution treated with potassium permanganate yields in the case of phenacetin a violet coloration

changing to dark ruby red, while in the case of acetanilid a green color is produced.

4. The hydrochloric solution of phenacetin diluted and treated with a weak solution of chromic acid, produces a red coloration. Acetanilid similarly treated yields at first a yellowish green and then a dark green solution in which potash produces a blue precipitate.

As previously mentioned, the formation of alcohol through treatment with caustic potash serves to distinguish phenacetin from acetanilid. Another test useful also in detecting small quantities of acetanilid in presence of phenacetin, is to treat the mixture with caustic soda or potash in the presence of chloroform, when, if acetanilid be present, the characteristic odor of isonitril is given off.

An excellent test for antifebrin in phenacetin and found by the writer to be most valuable is made with Plugge's reagent, a solution of mercurous nitrate with a little nitrous acid. The sample is boiled with a little water, then cooled and filtered. The filtrate is boiled with potassium nitrite and dilute nitric acid, then mixed with some of Plugge's reagent and again boiled. If no red color is obtained the sample may be considered as practically pure.

For the detection of para-phenetidin in phenacetin the following method is found to give the best results. 2.5 gms. of chloral hydrate are melted in a test tube on a water bath and then 0.5 gm. of the phenacetin to be tested is added. If the phenacetin is pure it will dissolve, forming a colorless solution which after prolonged digestion, however, acquires a pinkish tint. But if only a trace of para-phenetidin be present, the mixture will at once become dark violet to a reddish or bluish violet according to the amount of the impurity present.

Another excellent test for para-phenetidin is as follows : 0.5 gm. of phenacetin is dissolved in warm alcohol and five cc. of a solution of iodin in potassium iodid is added. The solidified mixture is then heated to boiling until the solution is complete. If para-phenetidin is present, a rose red color is produced which becomes more pronounced as the phenacetin recrystallizes.

It may be in place to speak of the more or less similar prepa-

rations which might possibly be confounded with phenacetin, such as exalgin, kairin, thallin, pyrodin, and salol.

The first, exalgin, or ortho-ethylacetanilid, $C_6H_4(CH_2)_2NH$ CH_2CO, is closely related to antifebrin. It melts at 101° C. and is very soluble in hot water.

Thallin, or tetra-hydroparaquinanisolsulfate, $C_9H_{10}NOCH_3H$, SO_4, is a white crystalline powder melting at 110° C., moderately soluble in water but difficultly soluble in cold alcohol.

Kairin or methyl tetra-hydroxyquinolinhydrochlorate, C_9H_{10} $NOCH_3HCLH_2O$, is a grayish or yellowish crystalline powder of phenol-like odor and saline taste. Kairin melts at 110° C., is moderately soluble in hot water and but difficultly soluble in alcohol or glycerin.

Pyrodin, acetylphenylhydrozin, $C_6H_5N_2H_2C_2H_3O$, as a commercial powder is very impure. The pure form is called hydracetin and is a white crystalline powder sparingly soluble in water and nearly tasteless.

Salol, phenylsalicylate, $C_6H_4(OH)COOC_6H_5$, is a white, tasteless powder with a slightly aromatic odor. It is insoluble in water but soluble in alcohol.

THE VANDENBERGH LABORATORY,
BUFFALO, N. Y.

THE ELECTROLYTIC ESTIMATION OF COPPER AS APPLIED TO INVERT-SUGAR DETERMINATIONS.

BY B. B. ROSS.

Within recent years numerous, as well as quite diverse methods have been proposed for the gravimetric determination of invert sugars by the determination of the amount of copper suboxid thrown down from the various cupric liquors employed in analytical work of this character.

The ease and accuracy of execution of the electrolytic process for the estimation of copper quite readily suggested the propriety of the adaptation of this method to invert-sugar determinations, and several processes have been recommended for the application of electrolysis to work of this description.

Some years since, Formanek (*Ztschr. Zucker-Ind. in Böh.*, 1890,

178; *Chem. Ztg. Rep.*, 1890, 41) advocated the electrolytic separation of the copper from a nitric acid solution, the process being conducted as follows: The precipitated suboxid, having been previously brought upon a Swedish filter paper and washed thoroughly, is dissolved on the filter with twenty cc. of nitric acid of 1.20 sp. gr., the filter being well washed immediately thereafter. The acid solution and washings, amounting in bulk to from 150 to 180 cc., are transferred to a platinum dish and the electrolysis of the solution is effected in the usual manner, a current yielding 3–4 cc. of oxyhydrogen gas per minute bring recommended for the work.

In the utilization of the process, as thus described, it has been found that the time and labor incident to dissolving the precipitates and thoroughly washing the filters constitute a not inconsiderable item where much work of this class is to be done, and the subsequent transfer of the liquid to another vessel still further adds to the work of manipulation.

In making numerous tests of the adaptability of the electrolytic method to invert-sugar determinations during the past year, it was found that the following modification of Formanek's method gave most satisfactory results.

The precipitation of the cuprous oxid is effected in a beaker and the precipitate is at once brought upon an asbestos filter in an ordinary funnel and the washing with hot water is performed in the usual manner. It will not be found necessary to completely transfer the precipitate to the filter, and when the washing is concluded, the filter and contents are placed in the original beaker and the funnel rinsed with a nitric acid solution containing four cc. of acid of 1.42 sp. gr. to 100 cc. of solution.

The dilute acid is added to the contents of the beaker until a bulk of about 200 cc. is secured, and after the platinum electrodes are placed in the liquid connection is made with a battery giving a current equivalent to 0.5 to 0.7 cc. of electrolytic gas per minute.

The anode employed is a flat spiral of platinum wire of the form devised by Luckow and is allowed to rest on the bottom of the beaker, while a platinum cylinder of the usual form, suspended vertically, receives the deposit of copper.

No attempt is made to dissolve the cuprous oxid, either on the filter or in the beaker, before the circuit is closed, it being found that the solution of the precipitate and the deposition of the copper proceeded simultaneously and continuously after the flow of current had commenced.

In order to test the accuracy of the results obtainable by this process, a solution of copper sulfate and also of alkali-tartrate were prepared according to Soxhlet's formula, the two liquids being preserved without mixing.

The accurately weighed equivalent of ten cc. of the copper sulfate solution was largely diluted with water, slightly acidified with nitric acid, and electrolysis of the liquid was accomplished in the usual manner.

Four separate determinations gave the following amounts of copper per ten cc. of solution.

Experiment No. 1 .... 0.1732 grams.
" " 2 .... 0.1735 "
" " 3 .... 0.1742 "
" " 4 .... 0.1740 "
Average .... 0.17372 "

A weighed quantity of the same solution, corresponding to ten cc., was next placed in a beaker, an equal volume of alkali-tartrate solution added, and the liquid, after dilution with water, brought to a brisk boil. A quantity of a pure dextrose solution, more than sufficient to completely precipitate the copper, was next added and the boiling continued for two minutes. The precipitated suboxid after a thorough washing upon the filter, was returned, along with the asbestos filter, to the beaker, about 200 cc. of dilute nitric acid solution added, and the electrolytic separation of the copper conducted as before described.

The results of six determinations executed in this manner · indicated the following quantities of copper per ten cc. of solution:

Experiment No. 1 ...... : .... 0.1730 grams.
" " 2 .... 0.1731 "
" " 3 .... 0.1736 "
" " 4 .... 0.1730 "
" " 5 .... 0.1737 "
" " 6 .... 0.1740 "
Average .... 0.1734 "

These figures attest the accuracy of the results to be secured by this method when it is properly executed, and numerous other practical tests with sugar products of various kinds further tend to confirm the conclusions drawn from these experiments.

A complete deposition of the copper can be readily secured in eight hours, and it was observed that the copper films obtained by this process were remarkably bright and entirely free from sponginess.

The extremely small amount of manipulation connected with the method causes little time to be consumed in its execution, and it is frequently found advantageous to allow the electrolytic separation of the copper to take place over night.

In addition to the use of the asbestos filter in an ordinary funnel, the Gooch crucible has been employed for some filtrations, the crucible, after completion of the washing, being suspended in a beaker containing dilute nitric acid, and connected with the positive pole of the battery.

It was found, however, that the time consumed by the process was much lengthened by the use of this last modification.

Where the cuprous oxid has been brought upon a Swedish filter paper instead of asbestos, the filter and contents can be placed in the beaker, and, after addition of dilute nitric acid, the electrolysis can be effected as before described.   It is also possible to conduct the electrolytic process with the use of a nitric acid solution even more dilute than the one to which reference has been made in the description of this method.

In addition to the employment of this process in the estimation of reducing sugars in different sugar products, it can also be readily applied to the determination of starch, where any of the leading cupric reducing methods are utilized after treatment of the starch containing materials with dilute acids.

THE CHEMISTRY OF THE GRAINER PIT.

BY THOS. PALMER, B.Sc., AND P. GERALD SANFORD, F.I.C.

The following experiments with the bate liquors used in the graining process may possibly not be altogether without interest to those chemists who are interested in the application of chemistry to the leather industry.

Three liquors were made. Liquor A represented 1121.5 gallons of an infusion of pigeons' dung, containing 6.187 pounds of air-dried pigeons' dung per gallon. Liquor B represented the same liquor after having been used as a grainer, and after it had been mended with 97 pounds of air-dried pigeons' dung dissolved in 91.62 gallons of water and fermented. Liquor C represented 984.5 gallons of residual liquor, *i. e.* after it had ceased to bring goods out.

Liquor A brought out 91 hides and 132 skins.
  "   B "   " 229 "   " 200 "
  "   C prepared 261 "   " 498 skins and 335 kips.

The whole of the dung paste, amounting to 240 pounds, used in making liquor A, contained 39.9 per cent. of material soluble in water, leaving 108 pounds of solid matter to go into solution. In the analysis of liquor A we could account for only 23.55 pounds, so that it would appear that a considerable amount, *viz.*, 84.50 of the organic matter, is destroyed during the process of fermentation to which the paste is subjected. The ammonia, as NH_3 present in 240 pounds of dung paste would amount to 3.144 pounds, whereas, the total amount found in the liquor was 3.808 pounds, showing a gain of 0.664 pounds of NH_3, which may be, we think, attributed to the decomposition of the organic matter during the process of fermentation. Liquor B, while measuring practically the same as A, was mended twice by the addition of 73 and 72½ pounds of dung paste, which gave on analysis 58.2 pounds of dry soluble material. On analyzing a sample of the liquor, 15.736 pounds was all that could be found; the amount of NH_3 added should have equalled $1.906 + 3.803 = 5.714$ pounds, whereas the quantity obtained was 6.272. This gain we attribute

to a further fermentative action, which had taken place during the period when the goods were in contact with the liquor.

ANALYSES.—PIGEON DUNG INFUSION.

	A.	B.	C.
Specific gravity	1001.2	1001.6	1001.4
Alkalinity (NH₃)	0.102	0.102	0.085
Total ammonia	0.034	0.056	0.025
Uric acid	none	none	none
Organic compounds } Tyrosene, etc. }	"	"	"
Total solid matter	0.210	0.350	0.330
Containing organic matter	0.074	0.186	0.162
" ash	0.136	0.164	0.168

ANALYSIS OF THE ASHES.

	Per cent.	Per cent.	Per cent.
Silica	0.004	0.003	0.003
Calcium carbonate	0.026	0.054	0.062
Magnesia (MgO)	0.008	0.007	0.004
Potassium carbonate	0.033	0.033	0.016
Sodium chlorid	0.065	0.067	0.083
Total	0.136	0.164	0.168

The residue of carbon left on filter contained

Organic matter ·········· 1.85 grains.
Mineral   "   ·········· 2.48   "

Total ··············· 4.33 grains = 69.28 grs. per gal.

The above 2.48 grains mineral matter consisted of

Alumina ··········· 0.154 grains.
CaCO₃ ············· 2.310   "
MgO ············· 0.016   "

Total mineral ···· 2.480 grains = 39.68 grs. per gal.

The analyses of the ashes are, we think, of much interest, though, so far as we are able to judge, the analysis fails totally to account for the action produced, and in this respect, as in others, we must probably look for physical rather than chemical causes for the effects produced. In this report, therefore, a study of the grainer vat by the aid of the microscope seems to show (1) that the quantity of active substances actually required is very small; (2) that waste of material is mainly due to the cause

that, in practice, the introduction of germs of disease is to a large extent unpreventable, though it is none the less equally clear that their action may be considerably diminished, seeing that the development of this class of organisms mainly depends on their requiring intimate contact with the air. The means hitherto adopted has been that of covering in the top of the grainer pit by means of flaps, or a light casing, so as to prevent in a measure the egress of the gases formed, and which, if the process is conducted in a partially immersed drum, causes a considerable saving both in time, labor, and materials.

That air is in any degree an essential feature in connection with this process is a complete mistake, as what takes place is a species or form of lactic, and hence of butyric, fermentation which, as shown by M. Pasteur, does not require oxygen for its support, but which depends on the presence of nitrogenous albuminoid matter in process of decomposition, a condition which depends on the degree of acidity of the liquor, *i. e.*, it must not exceed certain limits, a condition which does not arise in the grainer; as the substance necessary for saturation is being continually added, in more or less small quantities; that is, provided the goods are properly washed before going into the new grainer. The following series of experiments performed with some difficulty and after many unsuccessful attempts, will, we think, be found of considerable interest.

Into nine or ten liters of distilled water were put

```
Pure calcium lactate. ...................225  gms.
 "    ammonium phosphate ..............0.75 "
 "    potassium phosphate ..............0.40 "
 "    magnesium sulfate .................0.40 "
 "    ammonium sulfate..................0.20 "
```

The solution was clarified, when necessary, by the addition of a little ammonium phosphate and subsequent filtering.

The clear solution was now divided between several Pasteur flasks, of large size, which were then maintained at the boiling point for several hours, the bent tube from the flask being kept immersed in a basin containing some of the same liquid, also kept at boiling point ; when the flask had cooled, the end of the bent tube was transferred to a vessel of mercury, and the whole

apparatus was placed in a chamber at a temperature varying between 25° and 30° C. After being allowed to stand some time, in order to assure ourselves that all the germs of fermentation were rendered inactive, *i. e.*, that the liquids were sterilized, the liquids were impregnated with various cultivations, care being taken to do this out of contact with the air. The results, of course, depended upon the condition of the germs used for inoculation, as well as upon the quality of the medium introduced. In from six to eight days fermentation began to show itself by some minute bubbles becoming apparent in solution; in eighteen days those of larger size made their appearance in the solution, which rose to the surface of the liquid; from then till near the end of the experiment they came off in increasing numbers, especially from certain points on the bottom of the flask, where a deposit of earthy phosphates existed, while the liquid which at first had remained clear commenced to grow turbid. The results of the subsequent analysis of a portion of these liquors showed the entire absence of calcium lactate, and this, be it remarked, entirely *without* contact with the atmosphere; the butyric vibrios, after having exhausted all the oxygen in solution, falling inert to the bottom of the vessel, leaving the solution clear again. To determine how far a cure may be effected by simply closing in the pit containing the drum or paddle the following experiments were made.

Experiment A was conducted with a similar liquor to that already stated, some of which was inoculated with a pure dung infusion and left in large open cylinders containing about six liters each; some was left uninoculated but exposed to the atmosphere. In all cases very considerable fermentation ensued, as well as an abundant growth of bacteria, which formed a scoria, or film, on the surface and which, when examined under the microscope, was seen to be veritably swarming with living organisms. Some of these liquors, of both kinds, were now transferred to Pasteur flasks arranged over mercury as before stated, the boiling only being omitted, when fermentation proceeded with astonishing rapidity in both cases. In four days all signs had ceased. An analysis of the liquors showed that the whole of the calcium lactate had been consumed, not a vestige being left in solution.

Experiment B was conducted with a similar liquor as before, some was inoculated and some was left without inoculation, the whole being then divided between a set of boiling flasks the necks of which were loosely plugged with asbestos previously passed through the flame. Fermentation ensued in every case, though its speed was very materially reduced and there was a considerable diminishment of the scoria, and therefore germs of disease, though they were not altogether eliminated; their vitality however, appeared to be considerably affected by the atmosphere produced, and the liquors remained much clearer, especially those which were inoculated.

Experiment C. Some grainer liquor was now taken, and placed in a large boiling flask of ten liters capacity plugged with cotton wool, the liquor having previously been cleared from any thick matter by the addition of a little lime water and subsequent filtering; the whole was then kept at the temperature of the working grainer; in the mean time, a small beaker hung in the space between the wool and the top of the liquor was filled by means of a pipette with some of the liquor from a previous experiment. This liquor in the beaker was swarming with life. After several hours a noted change had taken place in the liquor in the beaker, the otherwise black or bluish liquor had become clear and of a pale, almost yellow, color. A deposit had formed, and the scoria had almost disappeared. This experiment, which appeared to be of some importance from a practical point of view, was repeated in a variety of ways, which space will not allow us to enter upon here. One thing appears certain, however, that the gases, emitted from a grainer during the time at which it is at work are capable of preventing the formation of an injurious organism in the bath or grainer. With this fact before him, one of us was induced to try what covering in the grainer pits with light match wood boarding would do, and the result arrived at was a considerable reduction in the quantity of material and the cost. 3.05 pounds of wet dung paste per hide, which would equal about 2 pounds of air-dried dung powder per hide, was found to give the same effect as 0.78 pounds of wet dung paste per hide, or about 0.5 pounds of air dried dung powder per hide. The mechanical portion of the work was carried out by immersed

drums revolving at a slow speed, the match boarding tops being put over all like a lean-to roof, closed at the sides, with flap doors in the center so as to allow of the goods being removed. We think that we have now produced enough evidence to show the advantage to be derived from an altogether simple arrangement like the one suggested, besides showing that the action proper of the grainer liquor is due to an organism, completely and entirely removed from the *bacteria*, in so far as they do not require atmospheric oxygen for their development.[1]

$$C_{12}H_{24}O_{12} = 4\,C_3H_6O_3$$
Milk sugar.   Lactic acid.
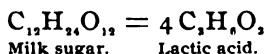
With bran drenches, or with a liquor akin thereto, the following interesting experiment was conducted:—A quantity of bran was put into a large size boiling flask (with sufficient water) where it was kept gently boiling for several hours. The hot liquor, previously clarified, was poured into a number of Pasteur flasks where it was again boiled; each was then allowed to cool, and as a means of precaution against the introduction of any germs the fine end of the long tube was plugged carefully with a small quantity of asbestos,—this at the very moment that the flame was removed from the flask, the asbestos itself having been first passed through the flame of a spirit lamp. It follows, therefore, that all the air that re-entered the flasks was deprived of any vital germs, consequently the solutions should keep indefinitely. To make quite certain that the manipulation was correct, the tubes used for inoculation were, in all cases, those that had been maintained at a temperature of 25° to 30° without changing, often for several months. When inoculation with pure butyric ferment was effected, the result obtained by the fermentive action was of a steady, constant nature, the liquor thickened and finally became clear again, all sugary bodies had disappeared, and where lactate of calcium had been added that too had done likewise; indeed, the fermentation could be renewed at once by simply adding a drop or two more of the calcium lactate solution. So far, then, we have dealt in this direction with pure inoculations and pure cultivations, that is to say, without contact with

[1] Bacillus acidi lactici. Crookshank Manuel of Bacteriology, p. 143, and W. B. Groves, Synopsis of Bacteria and Fungi.

the air, bacteria, and other forms of disease germs, which are therefore wholly eliminated. Suppose, however, we leave our infusion exposed for a few hours to the air, or allow the air in the flask to deposit its vital germs in our solution, vigorous fermentation ensues, which starts off at a gallop and stops equally as suddenly; our lactic compounds are equally destroyed it is true, but not by means of serviceable organisms, such as are required in the process of drenching; the consequence is that an excess of material, over and above that actually required, is necessary to counteract an otherwise harmful action. Some experiments have been made by us with regard to the practical elimination of these several forms of disease, which at first presented still more serious difficulties than in the case of the pigeon dung grainer.

H. Hoffman published in 1869 (*Annales des Sciences Naturelles*, V, 11) the following statement: "Aërobian bacteria lose all power of movement when suddenly plunged in carbonic acid gas. They recover it, however, as if they had been suffering from anæsthesia, as soon as they are brought into air again," and M. Pasteur has gone very deeply into the subject in his *Studies on Fermentation*.

As regards our experiments upon this subject, it may perhaps be desirable to state the results of one set which proved eminently satisfactory. Some of the pure unfermented liquor from one of the Pasteur flasks was sucked up into a previously heated and specially constructed live tube, which was then placed on the stage of the microscope. By causing the tube from this cell to pass into a tube containing an impure ferment, we could, by depressing the India-rubber ball at one end, get enough fluid up to infect the contents of the cell. This was done, and the cell kept warm by means of a hot stage and watched. In the space of a very short time, and working with a twelfth oil immersion objective, life very soon began to manifest itself in the shape of aërobian bacteria, which clustered round the various air bubbles which occurred between the top of the cell and the liquid in thick masses. Having satisfied ourselves thoroughly that we had some of the vibrios that we required, the India-rubber ball was removed, and after plunging the pointed end of the tube cell into a cup of

mercury the larger end was attached to a bottle in which carbon dioxid was being generated; pressure was prevented by vent being given to the generator. The effect was magical; the seething and struggling mass became motionless, apparently lifeless, at all events harmless to the liquid, until a bubble of oxygen was again admitted, when they revived after a time; at the same time it was easy to see that the development of the vibrios had not been in any way effected; but they in their turn would act in the same way should they be exposed to the atmosphere. Acting then on the information thus obtained, one of the bottles of liquid, to which had purposely been added some pure calcium lactate, was treated in the same manner,—that is to say, infected with an impure cultivation, an atmosphere above the liquid being maintained which was deadly to the aërobian bacteria, whilst providing always there was sufficient oxygen dissolved in the liquid, the fermentation proceeded as though the objectionable germs were altogether absent. Let us see then how far this can be practically applied to our drenches, for after all herein lies the practical issue of this process. Given a pit with sides of a certain depth, open at the top, there should be but little difficulty in getting enough gas on the surface of the liquor to entirely prevent the growth or development of any organisms which are harmful both to the goods and the liquor; the paddles, or drum, if used, should be so arranged that while at work it is wholly submerged. The hen or pigeon dung may be dried, being first freed from sand and other useless additions, when it may be powdered and mixed with sufficient bran to make the bath for any desired quantity of goods, of course taking the precaution to start the fermentation, in the first instance using the fermenting mass either for making or mending. This, of course, may be done in several ways, either by heating up the materials, straining or running off, allowing it to ferment as a liquor, or by fermenting the mass as a paste in a covered tube; portions of the paste being taken out as required, either for making or mending, when it should be put into a large sieve, and the soluble constituents washed out with warm water, the dross being rejected as useless, while the liquor runs by means of a shoot into the grainer pit. We have had many processes, from Turnbull's

down to Nesbitt's, which latter was rather a deliming process than a grainering one, but so many inventors fall foul of all really practical requirements. In the majority of works the old offensive process still holds its own.

LABORATORY, 20 CULLUM ST., E. C., LONDON.

ON THE OCCURRENCE OF PHOSPHATES IN NEBRASKA.

BY ELTON FULMER.

In the Republican Valley of Nebraska, one half mile east of Naponee, Franklin County, one of the small tributaries of the Republican river has given rise to the formation of two terraces. Their sloping sides are covered with grass and small shrubbery. At one point, on the farm of Samuel Gillard, the grass and soil have been removed from the side of the upper terrace, revealing the decomposed shale which underlies that region. In the immediate vicinity many varieties of rocks are found, all of which are more or less impregnated with iron. Their color, texture, and general character varies with the amount of iron present, and the combination in which it occurs.

The entire area of the decomposed shale exposed at the point above mentioned does not exceed twenty-five square feet. Every portion of it, however, contains blue nodules varying from one-sixteenth to one-fourth inch in diameter. Not only are the nodules found, but the blue material is disseminated in a more finely divided state throughout the rock.

The nodules have no apparent structure, are of irregular shape, some round, some oval, and many of them flattened. They are easily crushed to a powder with the fingers, lose water when dessicated over sulfuric acid, and change to a dark, reddish-brown color when ignited. When pulverized, they are easily soluble in mineral acids.

When an average sample of many of the nodules was submitted to a qualitative analysis, it was found that the essential constituents were ferrous and ferric iron, and phosphoric acid—hence a ferroso-ferric phosphate. This identified the mineral as the earthy variety of Vivianite, or "blue iron earth."

The mean of several quantitative analyses gave the following result :

<div align="center">

Phosphoric acid = 25.62 per cent.
Ferric oxid   = 15.67   "
Ferrous oxid   = 28.23   "
Water   = 23.95   "
Insoluble residue = 4.77   "

</div>

Small amounts of alumina, lime, and magnesia were present, but not estimated.   Deducting the insoluble residue, and calculating the rest to 100 per cent., we have the following percentage composition :

<div align="center">

Phosphoric acid = ·27.41 per cent.
Ferric oxid   = 16.76   "
Ferrous oxid   = 30.21   "
Water   = 25.62   "

</div>

This may be approximately represented by the formula $2(4FeO,P_2O_5) + 2Fe_2O_3,2P_2O_5 + 29H_2O$ which requires

<div align="center">

Phosphoric acid = 28.60 per cent.
Ferric oxid   = 16.11   "
Ferrous oxid   = 29.00   "
Water   = 26.28   "

</div>

According to this formula, the ferrous iron is in combination as basic ferrous phosphate.

No two samples of Vivianite, especially of the earthy variety, ever agree in composition, owing to the varying quantities of water present and the different degrees of oxidation.   The analysis nearest like the one above given, is reported of a sample of the earthy variety found at Allentown, New Jersey.

	Nebraska.	New Jersey.[*]
Phosphoric acid	27.41 per cent.	29.65 per cent.
Ferric oxid	16.76 "	18.45 "
Ferrous oxid	30.21 "	27.62 "
Water	25.62 "	25.60 "

About 250 feet from the point where the blue is exposed, another excavation has been made which reveals the shale in a more decomposed state—almost earthy—and containing *yellow* nodules, which are larger and more abundant than the blue. This excavation is about twenty feet deep and forty feet wide, and throughout the entire area thus exposed and the mass of material removed the yellow nodules occur in great abundance. Sometimes they are found as large as the fist, but are usually

* Watts' Dictionary of Chemistry. Vol. IV, p. 564.

found about the size of chestnuts. These are also very irregular in shape, and give no evidence of structure. Like the blue, they lose water by dessication over sulfuric acid, and become dark reddish-brown when ignited.

Some of these nodules are easily powdered between the fingers, while others are hard, more compact, frequently darker in color, and have a burned or baked appearance, suggesting the action of heat. They are all soluble in mineral acids, but with more diffculty than the blue. A qualitative analysis showed them to be a phosphate of iron, and that practically all the iron was in the the ferric condition.

The mean of the quantitative analyses gave the following result:

$$
\begin{aligned}
\text{Phosphoric Acid} &= 27.94 \text{ per cent.} \\
\text{Ferric oxid} &= 42.74 \quad `` \\
\text{Ferrous oxid} &= 0.32 \quad `` \\
\text{Water} &= 23.12 \quad `` \\
\text{Insoluble residue} &= 5.32 \quad ``
\end{aligned}
$$

Small amounts of alumina, lime, and magnesia were also present here. Deducting the insoluble residue, disregarding the small amount of ferrous iron and calculating to 100 per cent. gives the following:

$$
\begin{aligned}
\text{Phosphoric acid} &= 29.68 \text{ per cent.} \\
\text{Ferric oxid} &= 45.41 \quad `` \\
\text{Water} &= 24.56 \quad ``
\end{aligned}
$$

This may be approximately represented by the formula $4Fe_2O_3,3P_2O_5 + 20H_2O$, which requires

$$
\begin{aligned}
\text{Phosphoric acid} &= 29.87 \text{ per cent.} \\
\text{Ferric oxid} &= 44.88 \quad `` \\
\text{Water} &= 25.24 \quad ``
\end{aligned}
$$

Hence the yellow material is basic ferric phosphate.

It is interesting to note the abundance in which these two comparatively rare minerals occur, particularly in the portion of Nebraska above indicated, where so few minerals are found. The blue occurs in detached grains in Kansas, in small quantities in Missouri, but none reported from Colorado, Dakota, and Iowa. There is abundant ground for the statement that many tons of each kind exist here. The shale itself, where neither blue nor yellow is visible, carries varying amounts of iron and from one to three per cent. of phosphoric acid.

The peculiar interest, however, is attached not so much to their

occurrence or abundance, but to the relation which seems to exist between the blue and the yellow. As found now the blue nodules are smaller than the yellow; but there seems to be good evidence that the yellow ones were at one time blue. Many of them upon being broken, are found to be blue, bluish-green, or green on the interior; and wherever such coloration is found a portion of the iron is always in the ferrous condition. This fact, taken in connection with the close proximity of the two kinds to each other, the scoriaceous appearance of the rocks found near the yellow, and the baked appearance of many of the nodules, would seem to furnish a good foundation for believing that the yellow ferric phosphate has resulted from the practically complete oxidation of the blue ferroso-ferric phosphate; and suggests that heat may have been a factor in the oxidation process.

After a careful study of the minerals themselves, and an inspection of them *in situ* I am convinced that such is the case. It may be predicted that at some point between the two excavations, the mineral will be found in a state of oxidation intermediate between the blue and the yellow. It is hardly reasonable to suppose that the two varieties as studied and described will be found side by side.

A search through Dana and other mineralogical authorities fails to bring to light any statement of the occurrence of completely oxidized blue iron earth. Other hydrous ferric phosphates are described, but they are either in crystalline form or have a radiated structure, or other distinguishing physical characteristics which do not admit the yellow variety described to their class. In some cases yellow hydrous ferric phosphates, some basic and some normal, are described as being altered minerals such as Cacoxenite, Dufrenite, etc. But there is no evidence to show that the origin of this variety is from any of the minerals mentioned, while there is abundant evidence that it is a completely oxidized ferroso-ferric phosphate; or, in other words, Vivianite, in which the iron has been wholly changed to the ferric condition.

I do not believe such an occurrence has before been noted. This is my excuse for presenting it.

CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA.

SOME EXPERIMENTS ON AMERICAN OIL OF TURPENTINE. II.

BY J. H. LONG.

In the number of this Journal for January, 1892, I detailed the results of experiments on oil of turpentine, and chiefly with reference to tests for its purity. In this article I wish to take up the interesting question referred to in the former, *viz.*, the variations in the optical rotation of samples of oil of known purity. These variations are observed in all kinds of oil, but are probably most marked in that produced in the United States. The commercial mixed turpentines produced here always show a + rotation, but the variations in the specific rotation are much greater than those observed in the French or Russian oil, although the last named appears to be distilled in a manner which could scarcely be expected to yield a product of much uniformity. The French oil has always been distilled practically from one variety of pine, which in part accounts for the uniformity of the product obtained. Berthelot pointed out, however, (J. B., 1853, p. 519) that oils of somewhat different optical properties are obtained even from the same tree. In this country oils are distilled from trees of five or six different species, and this fact, alone, is of value in explaining the observed variations in the optical properties of commercial products.

When a sample of American oil, made by the usual steam distillation process, is subjected to fractional distillation in the laboratory, eighty-five per cent., or more, passes over below 163° C. in the first running. This usually consists chiefly of dextropinene. The portion boiling higher contains cymene and small amounts of oxygenated products.

It has been supposed that oil of turpentine undergoes marked changes on standing, especially when exposed to the air. To eliminate this source of error in my investigations I secured samples of the fresh "gum" directly from the turpentine camps and submitted them to distillation in the laboratory. This distillation was carried out in a copper still, the crude gum being mixed with an excess of water in order to prevent the formation of empyreumatic products by high degree of heat. The nearly pure

oil passed over with steam and gave a clear layer on the condensed water. It was then shaken with a weak solution of sodium carbonate to remove volatile acid bodies, washed ,with water, and then distilled over calcium chlorid. This gives a product of sweet, characteristic odor, without risk of altering the essential character of the hydrocarbons present by the preliminary treatment. The oils so obtained were tested as to their density and specific rotation with the results given below.

The densities were determined at 20° C. by an accurate Westphal balance, and the rotations by a large Landolt instrument (Schmidt and Haensch) using the 300 millimeter jacketed tube, kept at 20° by a stream of water.

Under the head of "description" in the table I give the marks which were on the samples when received from the producer.

No.	When Collected	Where Collected	Description.	Sp. gr.$^{20}_{4}$	a_D at 20° 300 mm.	$[a]_D$
1	Sept.,'90	Columbia, S. C.	Virgin dip.	0.8607	39.°690	15.°372
2	" "	" "	" scrape.	0.8613	48.745	18.865
3	" "	" "	Second year dip.	0.8616	43.534	16.842
4	" "	" "	" " scrape.	0.8618	35.960	13.908
5	" "	" "	Third " dip.	0.8605	49.016	18.944
6	" "	" "	" " scrape.	0.8638	—5.253	—2.027
7	June, '91	Wilmington, N. C.	Virgin dip.	0.8627	51.345	19.839
8	" "	" "	Second year dip.	0.8638	49.590	19.132
9	" "	" "	" " "	0.8619	22.065	8.339
10	" "	" "	Scrape.	0.8637	36.480	14.079
11	Aug., '91	Macon, Ga.	Spruce and yellow dip.	0.8620	13.150	5.085
12	" "	Mobile, Ala.	Yellow dip.	0.8620	41.854	16.183
13	" "	Wilmington, N. C.	Mixed scrape and dip.	0.8628	36.237	14.000
30	July, '91	Mobile, Ala.	Fourth year dip.	0.8631	50.721	19.589
31	" "	" "	Third " "	0.8640	40.325	15.557
32	" "	" "	Second " "	0.8640	20.360	9.889
33	" "	" "	Scrape.	0.8614	76.444	29.581
34	" "	" "	First year dip.	0.8615	45.620	17.652
36	Mch.,'92	" "	Yellow dip.	0.8602	64.811	25.114
37	" "	" "	Spruce dip.	0.8607	—89.930	—34.828
38	Apr.,'92	" "	" "	0.8612	—43.705	—16.916
39	" "	" "	Yellow dip.	0.8619	48.660	18.818
40	June, '92	" "	Second year dip.	———	16.780	(6.489)
41	" "	" "	Third " "	———	33.680	(13.025)
42	" "	" "	Scrape.	———	48.510	(18.760)

A number of commercial samples, known to be pure, may be included here. These samples were bought in Chicago and had

been in the hands of the dealers less than one year, in all cases, probably.

No.	Sp. gr. $\frac{20}{4}$	a_D at 20° 300 mm.	$[a]_D$
14	0.8650	31.°625	12.°188
15	0.8731	27.532	10.511
16	0.8653	25.225	9.717
17	0.8643	25.137	9.695
18	0.8643	30.240	11.662
19	0.8723	39.164	14.967
20	0.8639	35.483	13.693
21	0.8644	25.390	9.792
25	0.8632	38.690	14.941
26	0.8653	37.880	14.592
27	0.8632	33.402	12.900
29	0.8705	44.030	16.860
35	0.8650	40.504	15.607

These numbers disclose several interesting facts. They show that the natural mixed turpentine oils contain bodies with a higher specific rotation than is given by Tilden for pure "australene." His number, 21.5°, is entirely too low, as sample 33 in the above table gave $[a]_D = 29.581°$ and sample 36 gave $[a]_D = 25.114°$. It is also apparent that long exposure to the air on the tree does not lower the rotation, as in several samples designated "scrape" the rotation is unusually high, sample 33 being in the number.

From the above tables it is seen that we have an American turpentine with a negative rotation, a fact which confirms the prediction of Armstrong (*J. Soc. Chem. Ind.*, 1, 478, and elsewhere). This negative rotation was first noticed in sample 6, which was known to be a mixture of the product of several trees. Samples 37 and 38 were collected by my direction from spruce trees, and show a marked negative rotation, in one case greater than anything given by Tilden (Allen's *Com. Org. Anal.*, 2, 438) for the rotation of the commercial French oil. It would, of course, be unsafe to draw a conclusion from the examination of two samples, but the possibility is suggested by the results from the spruce turpentine that the low + rotation observed in many samples of American oils may be due to the presence of the product of spruce trees in the crude gum taken to the still. The

main portion of the gum is from the long leaf yellow pine
(*P. Australis*), but the spruce pine (*P. palustris*) is found in Ala-
bama, Mississippi, and occasionally in the Atlantic States.   In
collecting the gum no effort is made to keep the product of differ-
ent trees separate.   Samples 11 and 40 may have contained a
relatively large amount of gum from spruce trees.   After care-
fully fractionating distilled turpentine it will be noticed that the
first portions collected possess a higher (both + and —)rotation
than the last portions.   This is shown by results obtained with
samples 36 and 37, the redistillation being carried out several
weeks after the first one from the gum.   In each sample about·
400 cc. was taken for experiment and this was distilled in frac-
tions of about 75 cc. each.   The results are as follows:

NO. 36.

No. of fraction.	Boiling point.	Sp. gr. $\frac{20°}{4°}$	a_D at 20° 300 mm.	$[a]_D$
1	155.5–156.	0.8600	71.°250	27.°615
2	156. –156.5	0.8606	70.130	27.163
3	156.5–	0.8606	69.385	26.874
4	156.5–157.5	0.8609	65.875	25.506
5	157.5–160.	0.8630	56.715	21.906

A colored residue remained in the flask.

NO. 37.

No. of fraction.	Boiling point.	Sp. gr. $\frac{20°}{4°}$	a_D at 20° 300 mm.	$[a]_D$
1	156. –156.5	0.8602	—95.°085	—36.°847
2	156.5–157.	0.8605	—94.972	—36.790
3	157. –157.8	0.8610	—93.580	—36.230
4	157.8–159.	0.8613	—91.060	—35.242
5	159. –166.	0.8635	—83.674	—32.301

A colored residue remained in the flask.

The specific gravities of the higher fractions are apparently
increased during the process of distillation, but not enough to
seriously alter the specific rotations, which vary in an interesting
manner.   Somewhat similar results have been pointed out by
Marsh and Gardner (*J. Chem. Soc.*, 1891, p. 727).   The lower
rotation of the higher fractions is probably not due to the pres-
ence of oxygenated bodies, because, as will be shown below,
the same result is found after prolonged treatment with sodium

and distilling, and further because samples treated by the passage
of a current of air show a higher rather than a lower rotation, as
will be pointed out later. In one instance the last fraction
obtained by distillation gave a negative rotation. In this case a
liter of fresh oil was distilled and collected in twelve fractions of
75–80 cc. each. The results were as follows:

No. of fraction.	Boiling point	a_D at 20° 300 mm.
I	below 156.ᵛ	50.°35
2	at 156.	50.84
3	" 156.	50.05
4	to 156.2	48.72
5	" 156.4	47.29
6	" 156.6	45.40
7	" 156.8	43.25
8	" 157.1	39.64
9	" 157.5	35.69
10	" 159.0	28.20
11	" 166.0	13.68
12	" 175.0	—13.20

In another case, in which 350 cc. was fractionated into portions
of about 75 cc. each, the first fraction gave $a_D = 36.51°$ and the
fourth $a_D = 2.43°$. These experiments appear to suggest that the
substance of higher boiling point accompanying pinene in com-
mon American turpentine oil must have a negative rotation (see
L. Pesci, *Ber.*, **22**, ref. 108). Cymene, perhaps the most impor-
tant of these bodies, is commonly said to be inactive, but this
applies to the product prepared from camphor or from turpentine
by some destructive process. The natural product from cumin
oil was shown by Guareschi (*Ber.*, **6,** 758) and Pisati and
Paterno (*Ber.* **7,** 82) to be dextro-rotary. The specific rotation
was found by the last named chemists to be about $+ 4°$. It is
possible that the cymene from other sources, as turpentine, may
be laevo-rotatory.

<center>ACTION OF LIGHT.</center>

Armstrong and Pope (*J. Chem. Soc.*, June, 1891), and later,
Marsh and Gardner (*J. Chem. Soc.*, September 1891) have
shown that the rotation of American turpentine exposed to light

in the presence of moist air is increased. This may be due to the formation of sobrerol, the specific rotation of which is high and which is readily produced under the conditions named.

In several instances I exposed stoppered bottles of redistilled commercial turpentine to light for a period of twenty days or more, and observed always a slight increase in the specific rotation. No special precautions had been taken to dry the oils, however. In four cases the following values were found:

	$[a]_D$ original.	$[a]_D$ after 20 days.	$[a]_D$ after 50 days.
1	13.°69	13.°79	13.°85
2	14.01	14.12	14.21
3	5.°10	5.15	5.26
4	16.15	16.29	17.08

In the fourth case the increase is pronounced, and it is not probable that a trace of moisture in the oil with the few milligrams of air in the flask above its surface, could produce the oxygenated compound in quantity sufficient to change the rotation to this extent. Marsh and Gardner (*loc. cit.*) appear to think that light in presence of dry air is without action, but the experiment they cite (C, p. 727, *loc. cit.*) does not prove it.

They make no statement concerning the specific gravities of the oils examined, and without this datum it is not possible to calculate the specific rotations, the true basis of comparison. Their experiments only show that there is no *great* change.

ACTION OF AIR.

The absorptive power of turpentine for oxygen is a matter of great importance, and it is known that in some kinds this power is very marked. Kingzett has shown (*J. Soc. Chem. Ind.*, 1886, p. 7) that a very large amount of oxygen can be absorbed by passing air through warm Russian turpentine in presence of water, and it is a matter of common knowledge that other turpentines possess the same property, though in a less degree.

This combination with oxygen causes an increase in the specific rotation of the oil, as is well shown in the tables given by Kingzett. I have carried out a series of experiments with American turpentine in the same direction, drying the air, however,

and obtained the results given below. The pure, dry turpen-
tines described above were used for the purpose.

No.	$[a]_D$ original.	$[a]_D$ after cold air.	$[a]_D$ after hot air.
11	5.^{c}085	5.^{c}650	——
12	16.183	16.263	18.468
13	14.000	14.182	16.961
17	9.695	9.792	——
21	9.792	——	13.557

In experiment 11, air at 20° was passed sixty-five hours. In
12, air at 20° was passed sixty-five hours, and, in a fresh portion,
sixty-five hours at 90°. In 13, air at 20° was passed sixty-five
hours and through the same sixty-five hours longer at 90°. In
17, air at 20° was passed sixty hours. In 21, kept at 90°, air was
passed fifty-five hours. In all cases the air bubbled through rap-
idly and the containing flask was connected with a cold upright
condenser to collect the small amount volatilized. The table
shows the marked action at a high temperature while that at the
ordinary temperature is quite appreciable. After passage of the
warm air the samples became slightly yellow in color and showed
an increased specific gravity and higher boiling point on fraction-
ation. That hydrogen peroxid is developed in the air-oxida-
tion of turpentine is a well known fact. An important disinfecting
agent is made by the air-oxidation of Russian turpentine.

ACTION OF SODIUM.

Metallic sodium is without action on the pure hydrocarbons of
turpentine oil, but quickly becomes tarnished in the commercial
product, even when it is dry. If an excess of sodium is heated
with such turpentine out of contact with the air all action ceases
after a time, and when shaken free from a brownish-red layer of
oxidation product the metal remains bright. Heated in the air,
however, the action continues until the whole of the liquid, appa-
rently, is converted into a resin-like mass. Papasogli (J. B.,
1876, 400) calls attention to this behavior, but states that months
are required to complete the reaction.   •

I have not noticed that the removal of this product, when it is
produced by the treatment of the oil in closed vessels, alters the
rotation to any marked extent. This was tested by heating the

fractions obtained from samples 36 and 37, described above, with sodium out of contact with air until all action ceased. The metal was added to the fractions in thin wire and allowed to stand several weeks with frequent shaking before heating. After the last operation the fractions were allowed to stand until clear and polarized. The results in the 300 mm. tube were as follows:

No. of fraction.	Sample 36. a =	Sample 37. a =
1	71.°360	—94.°090
2	70.210	—93.931
3	69.464	—91.735
4	65.004	—90.600
5	55.500	—83.295

The rotations, alone, were determined here, but on comparing these with the former ones no important differences are found. The part removed, therefore, can have no marked action on polarized light.

ROTATION OF THE HYDROCHLORID, $C_{10}H_{16}HCL$.

According to the older observations and also to Landolt (Optisches Drehungsvermögen, p. 12) the hydrochlorid of dextro-pinene gives also a + rotation. Pesci (J. B. 1888, 900) and Wallach (J. B. 1889, 737) state that this compound is inactive, while that from the laevo-pinene has a strong — rotation. The values given for this rotation by the two chemists do not agree, however, and as both appear to have obtained their dextro-pinene from American turpentine the agreement here regarding the inactivity of the hydrochlorid may be accidental. As I have shown above, commercial American turpentine frequently contains a terpene of boiling point 156° and negative rotation, probably quite identical with that from the French oil. Such a mixture might readily yield an inactive hydrochlorid, and the low values given by Pesci for the specific rotation of the terpene isolated by him certainly suggest that he operated on a mixed product. • To further test this point a large quantity of the hydrochlorid was prepared from turpentine sample No. 35, for which the specific rotation was found to be $[a]_D = + 15.607°$. About five liters was taken for experiment. This was distilled

over sodium and then treated with dry HCl in the usual man-
ner, yielding an abundant crop of crystals. These crystals
were allowed to drain from the mother liquor, pressed out between
paper, and purified by crystallization from ninety-five per cent.
alcohol. The product so obtained was dissolved in similar
alcohol and allowed to crystallize a second time. The crystals
now secured were dried in warm air between porous plates. A
portion of ten gms. was weighed out and dissolved in pure alcohol
of ninety-six per cent. strength to make 100 cc. of solution. The
specific rotation determined from this was

$$[a]_D = + 6.733°$$

The whole remaining product was now dissolved in warm
ninety-five per cent. alcohol and allowed to crystallize slowly.
The first small fraction which separated out gave

$$[a]_D = 7.036°$$

The mother liquor was warmed gently to remove part of the
alcohol, and allowed to deposit again. After removing the crys-
tals which now formed, this operation was repeated several times.

A portion of the fourth fraction saved gave

$$[a]_D = + 6.733°$$

that is, the same as at first.

The compound must be looked upon as reasonably pure, and
while its specific rotation is much below that of the original tur-
pentine it is greater than that of several other turpentines given
in the first table. Assuming that the oil operated on contained
laevo-pinene and that the hydrochlorid from this is laevo-rotatory
it must follow from the above observations that the hydrochlorid
from pure dextro-pinene has even a greater + rotation. A small
amount of hydrochlorid made from another sample of oil was
found to have nearly the same specific rotation, but it is doubtless
true that different results would be obtained from oils which have
a much greater or much smaller rotation than that of sample 35.

A determination of the true specific rotation of this substance
would probably be found to be a matter of some difficulty, as its
solubility in most inactive liquids is not great. But the numbers
already secured are enough to show the fallacy of the conclusion
reached by Flawitzky (Ber., **15,** I, p. 5) regarding the constancy

of the relation between the molecular rotations of bodies and their simple derivatives.

Instead of the relation,

$$\frac{[C_{10}H_{16}]_D}{[C_{10}H_{16}HCl]_D} = \frac{136 \cdot 36,3}{172,5 \cdot 29,8} = \frac{4937}{5140} = .96,$$

or nearly 1.00, my determinations lead to a quotient nearly twice as large. New and accurate determinations with *unmixed* terpenes and their hydrochlorids will doubtless lead to a quotient different from unity, for both dextro and laevo-pinene.

My thanks are due to my colleague, Professor Powers, for valuable assistance in the purification of the compounds used.

CHICAGO, FEBRUARY, 1893.

METHOD OF DETERMINING PHOSPHORUS IN STEELS.[1]

BY C. B. DUDLEY AND F. N. PEASE.

OPERATION.

Put one gm. of the steel in a ten to twelve ounce Erlenmeyer flask and add seventy-five cc. of nitric acid (1.13 specific gravity). When solution is complete, boil one minute and then add ten cc. of oxidizing potassium permanganate solution. Boil until the pink color disappears and binoxid of manganese separates, remove from the heat and then add crystals of ferrous sulfate, free from phosphorus, with agitation until the solution clears up, adding as little excess as possible. Heat the clear solution to 185° Fahrenheit and add seventy-five cc. of molybdate solution, which is at a temperature of 80° Fahrenheit, close the flask with a rubber stopper and shake five minutes, keeping the flask so enclosed during the operation that it will lose heat very slowly.

Allow to stand five minutes for the precipitate to settle, and then filter through a nine cm. filter and wash with acid ammonium sulfate solution, until ammonium sulfid tested with the washings shows no change of color. Dissolve the yellow phospho-molybdate on the filter in five cc. of ammonia (90 sp. gr.) mixed with twenty-five cc. of water, allowing the solution to run back into

the same flask and thus dissolve any yellow precipitate adhering to it.   Wash until the washings and filtrate amount to 150 cc., then add ten cc. strong C. P. sulfuric acid and dilute to 200 cc. Now pass the liquid through a Jones Reductor or its equivalent, wash and dilute to 400 cc., and then titrate in the reductor flask with potassium permanganate solution.
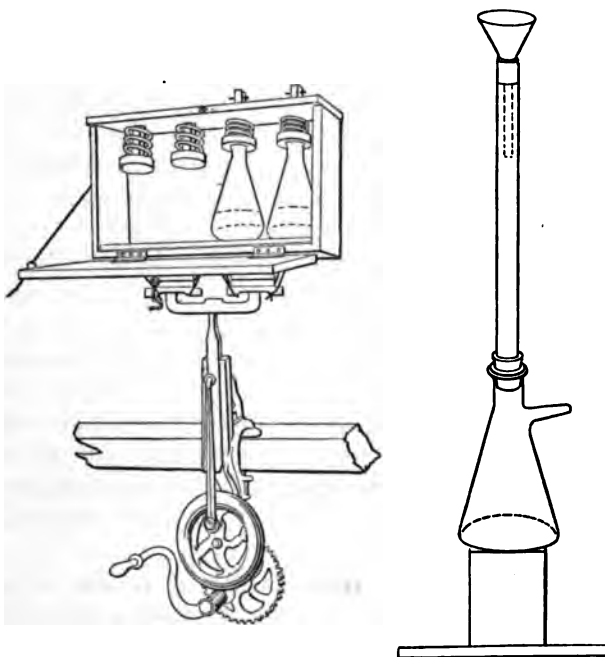
APPARATUS AND REAGENTS.

The apparatus required by this method needs no especial comment except perhaps the shaking apparatus and the modification of the Jones reductor.   Accompanying cuts illustrate these two. The shaking apparatus, as will be observed, is a modification of an ordinary milk shake machine, and is arranged to shake four flasks at a time, which is about all one operator can manipulate, without the solutions becoming too cold.   The cut is about one-twelfth the actual size of the apparatus.   The flasks containing the solutions rest on a sheet of India rubber about one-fourth inch

thick and are held in position by the coiled springs as shown. There is a recess in the spring arrangement to receive the cork of the flask. In the absence of a shaking apparatus the flasks may be wrapped in a towel and shaken by hand. Of course, during use the door of the box is closed, the cut showing it open so that the interior may be seen. The modified reductor seems to work equally as well as the more elaborate apparatus. The cut is about one-eighth actual size. As will be seen the tube is fitted with two rubber corks, the top one of which holds the funnel and the bottom one a small tube which also fits into the rubber cork in the flask. Next to the bottom cork in the tube is a disc of perforated platinum ; then about three-fourths of an inch of clean white sand; then another perforated platinum disc, and then the tube is nearly filled with powdered zinc. At least half the zinc may be used out before it is necessary to refill.

Burettes can usually be obtained in the market which are sufficiently well made and graduated with sufficient care, so that their error can be ignored. Of course this point should not be overlooked.

The specific gravities of the reagents given are essential, and the temperature at which the figures are correct is 59° Fahrenheit. In determining these gravities it is best to use a Westphal balance, but failing this, a sufficiently delicate hydrometer can be used.

The oxidizing permanganate of potash solution is made as follows: To two liters of water add twenty-five grams of C. P. crystallized permanganate of potash, and allow to settle before using. Keep in the dark.

The molybdate solution is made as follows: Dissolve 100 grams of molybdic acid in 400 cc. of ammonia (sp. gr. 0.96) and filter. Add the filtrate to 1000 cc. of nitric acid (sp. gr. 1.20). Allow to stand at least twenty-four hours before using.

The acid ammonium sulfate solution is made as follows: To one-half liter of water add $27\frac{1}{2}$ cc. of ammonia (0.96 sp. gr.) and then add twenty-four cc. strong C. P. sulfuric acid, and make up to one liter.

The permanganate of potash solution for titration is made as follows: To one liter of water add two grams of crystallized per-

manganate of potash, and allow to stand in the dark not less than a week before using. Determine the value of this solution in terms of metallic iron. For this purpose 150 to 200 mgms. of iron wire or mild steel are dissolved in dilute sulfuric acid (ten cc. of strong C. P. acid to forty cc. of water) in a long necked flask. After solution is complete, boil five to ten minutes, then dilute to 150 cc., pass the liquid through the reductor and wash, making the volume up to 200 cc. Now titrate with the permanganate solution. It is of course essential that the amount of iron in the wire or soft steel should be known. The standard in use in the Pennsylvania Railroad laboratory is a mild steel in which the iron is known by determining carbon, phosphorus, silica, sulfur, manganese, and copper, and deducting the sum of these from 100 per cent. Not less than two independent determinations should be made and three are better. The figures showing the value of the permanganate solution in terms of metallic iron should agree to a hundredth of a milligram in the different determinations. A very satisfactory method of making and keeping permanganate of potash solution is as follows : Have a large glass bottle holding say eight liters and two of half the size. Paint the outside of these bottles with several coats of black paint or varnish. Fill the large bottle with the standard solution, and after it has stood a proper time, fill one of the smaller bottles from it without shaking, and standardize. At the same time fill the second small bottle, and refill the large one. When the first small bottle is exhausted, standardize the second one and fill the first from the stock. When this is exhausted standardize the first again and fill the second from stock, refilling again the stock bottle and so on. By this means a constant supply of sufficiently matured permanganate is always available. Of course, if the consumption is very large, larger bottles or more of them may be required. Since changes of temperature affect the volume of all solutions, it is desirable that the permanganate solution should be used at the same temperature at which it was standardized. With the strength of solutions above recommended, if the permanganate is used at a temperature of 20° Fahrenheit different from that at which it was standardized, the error amounts to less than 0.001 per cent. on a steel containing 0.10 per cent. of phosphorus.

CALCULATIONS.

An example of all the calculations is given herewith. The soft steel employed in standardizing permanganate of potash solution in the Pennsylvania Railroad laboratory contains 99.27 per cent. metallic iron; 0.1498 gm. of this contains therefore (0.1498 x 0.9927) 0.1487064 gm. of metallic iron. This requires 42.99 cc. permanganate solution, or one cc. of permanganate solution is equal to (0.1487064÷42.9) 0.003466 metallic iron. But the same amount of permanganate solution used up in producing the characteristic reaction in this amount of metallic iron will be used up in reaction with 90.76 per cent. of the same amount of molybdic acid. Hence one cc. of permanganate solution is equivalent to (0.003466 x 0.9076) 0.003145 gram of molybdic acid. But in the yellow precipitate obtained as above described, the phosphorus is 1.90 per cent. of the molbydic acid. Hence one cc. of permanganate solution is equivalent to (0.003145 x 0.0190) 0.0000597 gm. of phosphorus. If therefore in any sample of steel tested as above, the yellow precipitate requires 8.6 cc. of permanganate, the amount of phosphorous in that steel is (0.0000597 x 8.6) 0.051 per cent.

NOTES AND PRECAUTIONS.

It will be observed that the method given above oxidizes the phosphorus in the iron by means of nitric acid, completes and perfects this oxidation and possibly neutralizes the effect of the carbon present by means of permanganate of potash, and then separates the phosphoric acid from the iron by means of molybdic acid. The molybdic acid in the yellow phospho-molbybdate is subsequently determined by means of permanganate of potash, the phosphorus being determined from its relation to the molybdic acid in this precipitate. The method given above applies to steel and wrought iron, but is not yet recommended for pig iron.

It is hardly necessary to say that all the chemicals and materials used in the analysis are assumed to be free from impurities that will injuriously affect the result.

1.13 specific gravity nitric acid apparently oxidizes the phosphorus just as successfully as a stronger one, while by its use solution is sufficiently rapid and there is less trouble during the subsequent filtration due to silica.

If the solution is boiled one minute after solution is complete it will use up much less permanganate than if the preliminary boiling is omitted.

Care should be taken to secure a crystallized ferrous sulfate free from phosphorus. The commercial salt is apt to be contaminated. It should be added in small crumbs so as to avoid excess. If too much has been used, a few drops of permanganate can be added to oxidize it.

The temperature at which the molybdate solution is added to the iron solution and the resulting temperature have an influence on the result. The directions should be closely followed, a good thermometer being used to determine temperatures. Never add the molybdate solution and then heat.

In washing the yellow precipitate it shows some disposition to crawl up to the top of the filter. Care should be taken therefore to have the filter fit the funnel so closely that even if the precipitate does crawl over the top it will not be lost while washing the filter completely to the top. It is very easy to leave enough molybdic acid in the top of the filter, even though the washings are tested, to cause an error of 0.005 per cent. in the determination.

The amount of molybdate solution given above is enough to convert all the iron into molybdate, and still leave enough to carry down the phosphorus.

It is best to make up molybdate solution frequently, as it slowly changes on standing. We think it unadvisable to use a molybdate solution over ten days old. It is best to keep the molybdate solution in the dark at a temperature not above 80° to 85° Fahrenheit. The solution should always be filtered before using. Much of the so-called molybdic acid of the market is molybdate of ammonium or molybdate of some other alkali. This fact cannot be ignored in making up the molybdate solution. A series of experiments with various molybdic acids and alkaline molybdates obtained in the market, indicates that if the amount of molybdic acid in the solution is that called for by the formula, irrespective of whether this amount is furnished by pure molybdic acid or any of the commercial molybdates referred to, the result will be much nearer the truth than if this is not done.

Good molybdic acid is best, but the alkaline molybdates can be used. The amount of molybdic acid in these molybdates can readily be determined by dissolving 0.1000 gram in 100 cc. of water to which a little ammonia has been added and filter. Now add ten cc. strong C. P. sulfuric acid, dilute to 200 cc., and pass through the reductor. Wash and dilute to 400 cc. and titrate with permanganate. The method given in the calculation above enables the amount of molybdic acid to be determined.

It is not advisable to make up the acid sulfate of ammonium solution for washing the yellow precipitate by using sulfate of ammonium and sulfuric acid, as the commercial sulfate of ammonium frequently contains phosphorus in some form.

The description and measurements given along with the cut of the modified reductor above will perhaps enable any one to make a suitable apparatus for himself if he desires. The powdered zinc used is that which will pass through a twenty-mesh sieve, and not pass through a thirty-mesh sieve. It may be obtained from Baker and Adamson, Easton, Pa. It is essential before using the reductor to pass two or three blanks through, containing all the materials except the substance being analyzed, and then titrate these blanks. The last two blanks should agree exactly, and the amount of permanganate used up by the last blank should be deducted from the final figure obtained on titration of the substance being analyzed. This preliminary preparation of the reductor is essential after a new charging with powdered zinc, and also equally essential after the reductor has stood idle even over night. The rate at which the material passes through the reductor can be controlled somewhat by the suction. The apparatus is very efficient and there seems little danger of too rapid a rate, but it is of course essential that the reduction should be complete. The properly reduced yellow precipitate solution should be green or slightly so, depending on the amount of molybdic acid present. A trace of "port wine" color in the reduced solution before titration with the permanganate indicates lack of complete reduction and renders the results of the analysis doubtful. In case of incomplete reduction pass the liquid through the reductor again. If the rate is somewhat slow and the solution being reduced some-

what warm, hydrogen gas enough may be generated to throw some of the liquid up against the sides of the tube above the zinc, and also bubble up through the liquid in the funnel. Care should be taken that this latter does not result in loss, and that the liquid adhering to the sides of the tube is removed by the subsequent washing.

There is some analytical evidence when using the method described above, that a portion at least of the arsenic which may be present in a sample of steel under examination, is precipitated along with the phosphorus, and counts as such in the final result. Until some simpler method of overcoming this difficulty than any at present known has been devised, and until the injurious effect of arsenic on steel has been demonstrated to be so small that arsenic can safely be ignored, the results obtained by the above method will be regarded as the phosphorus content of the various steels purchased in accordance with Pennsylvania Railroad specifications.

Samples of steel in which the phosphorus has been determined will be sent to parties asking for the same in order to enable them to make such comparisons as they may desire.

In formulating the method given above, the published work of Emerton, Wood, Drown, Hundeshagen, Colby, Shimer, Handy, and Jones, has been freely consulted and used. It would be difficult to state in detail what is due to each.

PATENTS OF INTEREST TO CHEMISTS.
EDITED BY A. H. WELLES.

Orrin B. Peck has a number of patents on a centrifugal ore separator (489,090, 489,197 to 489,205, and 490,084), and 490,041, a centrifugal amalgamator. Nos. 489,744, 490,849, and 490,850 were granted Geo. Johnston for an ore concentrator; 490,911 to Wilhelm Krug for an ore separator; 489,538 to William S. Lockhart and E. W. Streeter for a hydraulic mineral separating apparatus; 489,797 to Charles Faber for an ore washing machine; and 489,101 to Chas. E. Seymour, for an ore separator.

James Greenwood patents an apparatus for the production of chlorin and caustic soda by electrolysis (489,677), and Leopold

Le Blois a method and apparatus for bleaching or dyeing textile materials (489,819). Bruno Beyer treats silk waste to the action of oil-soap, cold water, and salt steam baths, drys, and then subjects to the action of potassium permanganate (489,919). Two new dyes are patented, one (489,623) by Fritz Bender, a "yellow-red" dye, by oxidizing the bluish-red dye stuffs derived from dialkylmeta-amido phenols; the other (490,408), by Albert Herrmann, a new color derived from tetralkyl-diamido-triphenyl carbinols, a copper red powder wlth metallic luster, "soluble in water, insoluble in alcohol and benzine, dyeing wool and silk in acid bath very uniform blue shades." Joseph Berlinerblaü (489,728) prepares para-phenetol carbamide by treating para-phenetidin or para-anisidin with phosgene, adding ammonia to the products, and crystallizing out the resulting compound. R. P. Pictet (489,552) purifies commercial chloroform by cooling to 80–82°, filtering the cold mass, crystallizing the chloroform, separating the non-crystallizable part, and finally distilling the chloroform at a very low temperature, and collecting the middle products. Byron B. Goldsmith produces nitro-cellulose or celluloid surfaces by coating with pyroxylin varnish and varnishes containing resin (490,195). 489,879 is granted Carl Steffen for a process for obtaining sugar. 490,538 is a process for preparing raw grain proposed by H. T. Brown. 490,056, Otto Zwietusch, patentee, is a process for making beer, and Arnold Kreusler (489,018) also has a new method of obtaining the same beverage, and E. A. Spink ages liquors in an original way (489,337). Pepsin, gumarabic, and alum are claimed by S. C. Wilson (489,775) as a compound for increasing the yield of butter from milk, and David W. Hudson *et. al.* proposes (489,814) to manufacture a so-called butter containing pure butter, sweet milk, and oil of cocoanut. Should the cholera come this year, as is feared, Albert E. Woolf's disinfectant and deodorizer (490,797) ought to be a valuable one, containing as it does "chlorin, chlorids, hypochlorites, free oxygen, and ozone." What more could one desire?

A composition for leather for razor straps consisting of tallow, beeswax, molasses, and chimney ashes from burnt coal is the idea of Frank Minnis (490,030). Matthew H. Devey uses powdered

slag, glass and a binding medium for an insulating compound (490,641). George S. Lee (490,667) is granted the right to use "asphaltum, distilled coal-tar, residuum of petroleum, disintegrated paper, or wood pulp, and air-slaked lime" for the ingredients for a patent pavement. Vinegar, lime-water, salt, alum, white vitriol, linseed or other drying oil, and petroleum is the combination Richard J. Doyle uses (490,547) for a non-inflammable paint, and the same combination with the addition of from twenty-five to eighty-five per cent. of aluminum silicate in the form of soft unctuous clay (490,548) is used for a non-inflammable cement.

That indefatigable worker, Thos. A. Edison, has an improvement (490,954) in the manufacture of carbon filaments for electric lamps. Jean M. Raymond first soaks vulcanized rubber in ·benzine, then immerses in a solution of permanganate of potassium, and then treats again with benzine in order to render the rubber adhesive (490,500). To unhair hides, a composition of "fifteen pounds of hydrated sulfid of soda, white creosote, eight ounces carbolic acid, four pounds of fifty per cent. Baumé solution," is used by Jacob Mellinger, (490,791). Herman Endemann is the patentee of a composition for artificial stone (489,377). Magnesia, magnesium hydrate, basic oxalate of magnesium, and sand are named. Finely ground mica is used as the base, which combined with oil, a pigment, and a binder forms a paint compound introduced by W. B. Abert (491,003).

Samuel Rodgers patents a detonating compound (489,761) which contains potassium picrate and chlorate, extract of logwood and a·gallotannic ink; and Prof. C. E. Munroe, 489,684, extracts "the lower products of nitration from gun cotton, which is mixed and incorporated with nitro-benzene, and indurated by acting upon it with heated liquor vapor," to form an explosive powder. 490,612, a lime slaking machine, is the invention of A. R. Miller and 490,437, is a hydrogen gas generator devised by William and Thos. Hawkins. F. H. and R. H. Piekles purify pyrolignites by treating a liquid pyrolignite with a prussiate residue, raising the temperature at the same time to the boiling point, and separating the combined insoluble matters (490,497). To make fertilizer from tank water, O. T. Joslin (489,010)

evaporates the water to a thick syrup, adds a small per cent. of sulfuric acid and from five to twenty per cent. of magnesium sulfate, absorbs the supernatant liquid with some suitable substance and dries the mass at 300°–400° F. and grinds.

W. P. Miller patents a process for recovering precious metals (492,040) which is mechanical in its application; while John Blair places gold ores, saturated with a solution of sodium chlorid and nitrate, in a perforated vessel, in a solution of sulfuric acid, and the soluble parts are washed back into the acid (492,133). Carl Moldenhauer treats ores bearing gold with a solution of potassium cyanid in the presence of potassium ferri-cyanid (492,221). Samuel H. Cochran also patents a process for separating the noble from the base metals (491,638.) Antoine P. G. Rollet is the inventor of a process of purifying pig iron, which consists in mixing the iron with fuel, limestone, fluor-spar and iron oxid, subjecting the mixture to the action of a blast and separating the refined iron (491,498) while 491,508 is the patent on the cupola furnace in which the operation is carried on. To convert malleable iron into steel, A. J. Hindermeyer uses plumbago, salt, and sulfuric acid (492,679), and to separate tin from iron and steel Thomos Twynam first coats the surface of the tin with a special preparation, then oxidizes the metal and separates it from the iron (491,254). John J. Crooke frees copper and lead from foreign metals by fusing, then heating in an air blast to form oxids, and while fused, adding ammonium chlorid and finely divided carbon (491,084). A furnace for "roasting, calcining, and oxidizing metals and their compounds," invented by Herman Frasch, is protected by 492,551, and 491,274 is granted Thomas Thomas for a desulfurizing furnace. A. Crossley has also a furnace for producing ferro-ferric and ferric oxids (491,085).

Thomas L. Wilson has two patents. 491,394 is on a process for electrically reducing aluminum and forming alloys from the metal. Alumina is electrolyzed, the anode consisting of molten base metal and the cathode of carbon, in the presence of finely divided carbon, the reduced aluminum uniting with the base metal to form an alloy. 492,377 is an electrical process for reducing refractory metallic ores. "Production of Artificial Crystalline Carbonaceous Materials" is the high-sounding name given to

a method for preparing silicid of carbon, Edward G. Acheson, patentee (492,767); substances containing carbon, silicon, free or combined, and a chlorid of an alkali metal are subjected to the electric current. Emile Denorus (491,799) has a novel solution for electro-plating, consisting of snail albumen and silver nitrate, in which the article to be coated is first dipped.

John E. Chaster (492,711), Fred. O. Norton (491,686), and Charles C. Ormsby (492,425) have each patented an ore amalgamator, while the last also covers his process by 492,426. Orrin B. Peck has a "machine for centrifugally treating molten materials" (491,131), and Adolph Schulenberg an ore-crushing mortar (492,634).

For the preparation of pure carbon dioxid, E. Luhmann leads gases containing carbonic acid into sodium phosphate and heats to liberate the carbon dioxid (491,365). Henry C. Higginson describes a new apparatus for the manufacture of whiting (491,353), and Godfrey L. Cabot (491,923) has an improved process for producing lamp black. Henry Blackman (492,382) describes an apparatus for recovering alkali, and Ludwig Mond (491,741) has an original form of apparatus for volatilizing ammonium chlorid, zinc chlorid and antimony being filled into the bottom of the retort which is exposed to the direct flame, while the ammonium chlorid is fed from above through a hopper.

Henry Gall and another compatriot patent an electrolytic process for the manufacture of the chlorates of the alkaline metals and metals of the alkaline earths from the corresponding chlorid, (492,003) this making the sixth nation which has granted them a patent. E. B. Cutten (491,699) protects himself in a method for preparing liquid chlorin; 491,700 covers his invention for electrolytically producing soda and chlorin; and 491,701 for producing potassium chlorate by electrolysis.

Oscar Guttmann, makes nitric acid by forming gaseous nitric acid in a distilling chamber, conducting it in a tube to a condenser and introducing an air-blast into the tube to act upon the gaseous nitric acid before condensation (491,481). Paul Bronner (491.635) digests crude lead sulfate with sulfuric acid, washes, treats with sodium carbonate, washes, dries and heats in a muffle the carbonate of lead thus obtained, digests the pure oxid of lead

with lead acetate and precipitates with carbon dioxid to produce white lead. William M. Brewer (491,074) burns clay, then grinds it to powder and mixes with it one-third its bulk of raw or unburnt clay, and finally adds glass, sand, flint, slaked lime, and common salt, when it is stored away and tempered for use in making pottery-ware.

A. Hummel has a new process for the manufacture of beer (492,292), C. Heintz, a method and apparatus for purifying and softening liquors (492,542), R. Rahr a process for making caramel malt (491,813), and Simeon L. West has an apparatus for purifying, sterilizing and filtering drinking water or other potable liquids (491,828).

Professor Peter T. Austen incorporates an alkaline nitrate with logwood extract, producing thereby a friable solid, soluble in cold and very soluble in hot water (491,972). He uses a similar method in preparing a solid coloring matter from fustic (492,368). Then Robert Gnehm and Jakob Schmid introduce a new brown dye (491,422), the sodium salt of an azo-derivate of meta-diazo-benzoic acid and Bismarck brown ; Theodore Diehl derives a new blue-black azo dye (491,410), Jakob Schmid and Johannes Mohler, a new violet-blue induline dye, prepared by melting a mixture of para-phenylene-diamine, hydrochlorate of para- phenylene-diamine, and alpha nitro-naphthylamine at 160° to 190°, dissolving the melt in hydrochloric acid and precipitating with common salt (491,378). Frank P. Pearson (491,951) and George Donald (491,961) patent processes for printing colors with aniline black, as well as Wm. Browning (491,673).

[The specification and drawing of any U. S. Patent in print may be obtained from the publisher of this Journal. Applications must be accompanied in all cases by twenty-five cents for each patent specification wanted. BE CAREFUL TO WRITE THE NUMBER LEGIBLY.]

ERRATA.

In the article by S. H. Emmens, under table IV, p. 649, November, 1892, the figures 0.06 and 0.68, under columns headed Fe and Cu, sixth line from foot of table, should be transposed.

In the article by R. D. Campbell in the issue for January, 1893, page 2, the third line from bottom should read " 0.1 per cent." instead of " 0.100 gm." of arsenic.
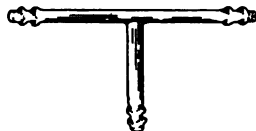
SOME NEW FORMS OF APPARATUS.

BY EDWARD B. VOORHEES AND LOUIS A. VOORHEES.

A WATER OVEN FOR DRYING IN HYDROGEN.

HE method for the determination of moisture in cattle foods, as adopted by the Association of Official Agricultural Chemists, requires the drying of the substance for five hours, at the temperature of boiling water, in a current of dry hydrogen, without allowing the vessel containing it to come in contact with the boiling water. The apparatus devised by the writers to meet these requirements may be briefly described as a double walled water oven of copper, opening at the top by a heavy brass lid, which screws down upon a rubber gasket; and with the inner wall removable from the outer for the more convenient opening and closing of the apparatus.

The cylindrical tank A forms the outer wall of the bath and holds the boiling water; it is nine inches high. The inner wall consists of B, also cylindrical, six inches in diameter and seven and one-half inches high. By placing B inside of A the water oven is complete. The lid to the inner vessel is shown at c; the brass posts in the lid at ff are for greater facility in the screwing and unscrewing; at k a thermometer may be inserted; at hh are the openings for the passage of the hydrogen, one through the lid, and the other through the side near the bottom by means of the tube e; around B near its top is the flange x, of

such a width as to cover A when the apparatus is put together; the bottom of B is then four and one-half inches from the bottom of A, and by its weight as well as by slot fastenings, one of which is shown at *s*, and which are caught by pins inside of A, B is prevented from floating out of A when the space between them is three-fourths filled with water. The entire apparatus is placed directly upon a gas stove, by means of which the water in A is caused to boil.
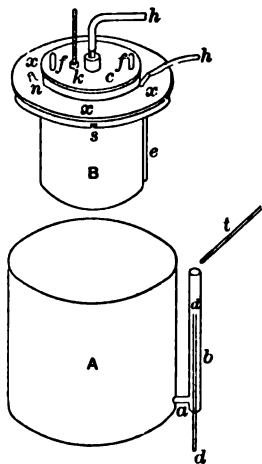

Fig. 1.

Tests with an accurate thermometer, which has been proved by comparison with standards, have shown that the temperature of the interior of this water oven reaches that of the boiling water, which is not the case with many water ovens which open at the side; the observed temperature varied from 99.5° to 100° C., according to barometric pressure, and, furthermore, was not reduced by the hydrogen current, no matter what its rapidity.

Inasmuch as the fat is subsequently extracted from the dried samples, the substances are dried in fat extraction tubes. These are of ⅞ inch glass tubing, five and a half inches long, capped at the end with fine copper gauze, upon which a plug of asbestos is laid in the same manner as in the Gooch crucible.

The tubes are held upright in a rack which fits inside the inner vessel. In the drying the current of hydrogen diffuses through the sample instead of being forced through, and in subsequently passing through sulfuric acid occasions no blackening, due to the mechanical transferrence of the substance. Twelve samples are usually dried at a time, although the rack will hold eighteen; racks are also provided for holding crucibles and flasks.

During the drying the water in the bath is kept at constant level, without effect upon its temperature, by a device which has been previously used on other water ovens. The tube *a* (Fig. 1) connects the bath and the tube *b*; the level of the water is therefore the same in each. Water from a reservoir constantly drops

in the latter from the tube *t*, and any excess over the amount of evaporation escapes by the overflow *d d*. At the expiration of the drying the bath and contents are rapidly cooled in hydrogen by a current of cold water entering the water compartment by the steam escape *n* and passing out by means of the arrangement last described. After half an hour of cooling, the lid may be unscrewed, the inner vessel having been lifted out for greater convenience; the rack with the samples is then placed under a bell jar until the hydrogen is diffused, and the weights then taken.

A full and constant supply of hydrogen is secured from a Kipp generator of moderate size (twenty inches in height) through the agency of the simple device represented in Fig. 2. The bottles have a capacity of two liters. At the start number 1 is filled with water to displace the air ; as soon as the generator is in regular action, and delivering hydrogen unmixed with air, the pinch cock at *a* is removed ; the hydrogen then forces the water from the first bottle into the second. The caliber of all the tubes is small, so that this takes place with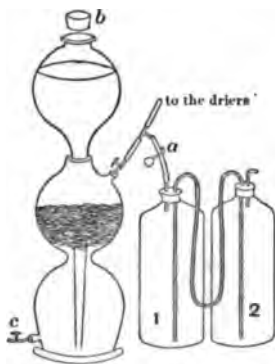out diminution of the current through the water oven. When bottle number 1 is nearly full of hydrogen, the pinch cock is replaced and the supply of hydrogen for the drying of the samples is taken in the usual manner direct from the generator. As soon as the acid in the latter begins to lose its efficiency, bottle number 2, which now contains most of the water, is elevated upon a shelf, thereby putting the hydrogen in number 1 under pressure. The stopper *b* is inserted, pinch cock *a* is removed and cock *c* is opened. The hydrogen from the bottle now supplies the current for the samples which are drying, and also forces the spent acid out of the generator, while the stopper *b* prevents any movement of the contents of the upper bulb. By closing cock *c*, replacing pinch cock *a*, removing stopper *b*, and adding fresh acid at the top, the generator is again working regularly, and bottle number 1 may be refilled with hydrogen.

to the driers

Fig. 2.

The drying of the hydrogen is effected by causing it to bubble through four separate portions of sulfuric acid,. 66° Baumé.

APPARATUS FOR FAT EXTRACTION.

In the apparatus presented in the accompanying illustration, the well known principle of the continuous extracter is adopted ; originality, therefore, is confin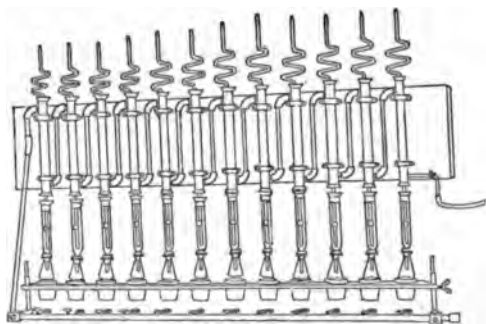ed to the details of the application, whereby compactness and convenience in handling are secured. The volatilization of the ether in the flask, to subsequently condense above and pass through the sample in the inner tube, carrying the fat with it into the flask again, needs no description.

Fig. 3.

A main feature is the arrangement of the cups in which the flasks are immersed in water and of the burners by means of which the water is heated. All of these are fastened together, and the distance of the lights from the bottoms of the cups is adjustable, but when once adjusted the whole frame of lights and cups may be raised or lowered together on the supports at the ends.

The condensers are of iron piping one and one-fourth inch in diameter, closed at the ends with rubber stoppers perforated to admit the passage of the glass tubes ; they are all connected together by iron piping of three-quarters of an inch diameter. A single stream of water effects the cooling.[1]

With the exception of the rubber stoppers in the condensers, corks are used as being in the end the most satisfactory. If carefully selected they will last several seasons without replacing. If the inner tubes are for the extraction of fodders, a tapering form at the lower ends will effectually prevent the rising of the substance during the extraction. By the substitution of siphon

[1] A similar form of condensers is used in the distillation of ammonia in the determination of nitrogen by the Kjeldahl method. with equally satisfactory results.

tubes, the apparatus is adapted for the determination of fat in milk by Adams' method, in which case the angles at the top of the condensers are efficient in preventing the loss of ether.

The apparatus is but eight inches deep, stands close up to the wall and thus leaves considerable working space in front upon the table upon which it is placed.

A BATH FOR THE DIGESTION OF PHOSPHATES IN AMMONIUM CITRATE.

This apparatus consists of a rectangular copper tank, eighteen inches long, twelve inches wide and five inches deep, in which the water is contained and heated from beneath by Bunsen burners. Fitting loosely inside the tank is the wooden frame *a* shown in the figure. The board *b* is twelve and one-half inches long and six and one-half inches wide, and fills the open space inside the frame *a*. Both frame and board are an inch in thickness and float upon the water. The dimensions here given are for these pieces in their water soaked and consequently swollen condition. They are then of sufficient weight also, to immerse to the neck twelve flasks of 150 cc. capacity, two-thirds full of ammonium citrate solution. These are held in the slots, the shape of which allows the operator to agitate them and yet holds them safely when the inner board is temporarily out. The temperature is controlled with a thermometer inserted through a hole in the board *b*. The covering of the entire surface of the hot water with a non-conducting material maintains the required temperature for half an hour almost without assistance.
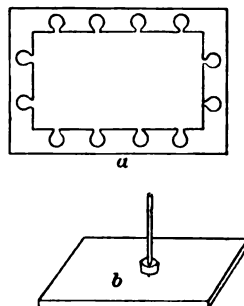

Fig. 4.

PIPETTES OF SPECIAL VOLUME FOR THE SIMPLIFICATION OF CALCULATIONS.

The conversion of the results of the balance into results per centum in the case of those substances not weighed in the form reported, has usually occasioned considerable clerical labor, even when tables are employed. To obviate this labor in the case of

phosphoric acid, potash, and chlorin—the main determinations of this character at this laboratory—pipettes of special volume have been used with entirely satisfactory results. When definite weights are taken and their solutions made up to definite volumes, these pipettes deliver an amount of original substance equal to the conversion factor divided by an integer, which latter by cancellation becomes the multiplier. The weights and volumes to be taken are those stated in the methods of the Association of Official Agricultural Chemists; the theoretical volumes of the pipettes and the method of procedure are given in tabular form :—

For the determination of	Weight of substance taken, gm.	Volume of solution, cc.	Volume of pipette, cc.	Substance delivered by pipette, gm.	Conversion factor.	New factor.
Total phosphoric acid	2.	200	63.965	0.63965	63.965	100
Insoluble '' ''	2.	100	63.965	1.27930	63.995	50
Soluble '' ''	2.	300	47.974	0.31983	63.965	200
Potash	10.	500	48.270	0.96540	19.308	20
Chlorin	10.	500	49.452	0.98904	24.276	25

Thus, if the solution of two gms. of material be diluted to 200 cc. and 63.965 cc. (practically 64 cc.) taken for the determination of total phosphoric acid, the actual weight of magnesium pyrophosphate only needs its decimal point moved two places to the right to read per cent. In the case of soluble phosphoric acid and of potash, a multiplication by two accompanies the displacement, which in the latter consists of but one decimal place. With the determinations of insoluble phosphoric acid and chlorin the multiplications may be made as indicated, but a better course is to move the decimal point two places to the right and divide by two and four respectively, an easy mental calculation performed more quickly than the result can be written.

A MEANS OF TRANSFERRING WASH SOLUTIONS.

The usual manner of overcoming the labor incidental to transferring large quantities of wash solutions by means of the ordinary wash bottle is to elevate the solution and employ the head thus obtained; the stream is brought down to the work by tubing and then controlled by a pinch-cock just back of the jet in the end.

When much work is to be done the advantages of the method
are obvious; not only are the muscles of the mouth and cheeks
relieved from the labor of blowing, but the muscles of the back
also are relieved from the fatigue of stooping. Furthermore the
stream is instantly smooth and not interrupted by those few
small bubbles of air which are usual in the ordinary wash bottle.
But a disadvantage of the method is the lifting of each individual
solution up to a height, and down again when the work is done;
or if left elevated until used up, their tubes are constantly under
pressure with consequent danger of leaks, disagreeable in them-
selves and, in the case of ammonia wash, ruining other work
requiring an ammonia-free atmosphere which may be going on,—
potash determinations for example.

To overcome this objection and still secure the advantageous
features of gravity washing an arrangement was
devised whereby the wash solutions are handled
in exactly the same manner as before, but are
moved through the agency of compressed air,
which is itself secured by the gravity of water.

The tube $a\,b$ is kept full and gently overflowing
with water by connection at a with the city sup-
ply, the excess being conducted to the drain
through the pipe $c\,d$. When the cock e is
opened the tube $a\,b$ tends to empty itself into
the large bottle F, which at the start is full of
air. The air is consequently under pressure to
a degree determined by the height of the column
of water in $a\,b$ and the pressure under which it
is flowing out at b. This compressed air is con-
ducted by one-fourth inch lead tubing to various
convenient parts of the laboratory where any
bottle with the customary short and long tubes

Fig. 5.

may be attached by its short tube, and the wash water delivered
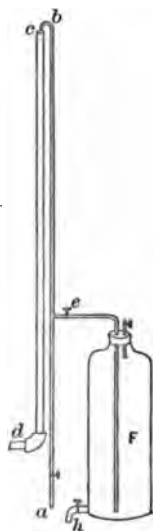through a hose as before described.

The two pipes may be conveniently fastened on the wall near
the sink, while the bottle may have a shelf provided or even
stand upon the floor. The size of this bottle depends upon the
amount of work to be done. With no leaks of air throughout

the apparatus, it need be but a little larger than the amount of wash water to be handled. In this laboratory it is sufficient for a half day's continuous using, after which it is allowed to drain into the sink by the cock h at the bottom. Pressure is thus relieved when the apparatus is not in use, while the bottles containing the wash solutions, being near at hand, may be disconnected and stoppered.

NEW JERSEY STATE AGRICULTURAL
  EXPERIMENT STATION.

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND J. COLEMAN SALTAR.

1.   SEPARATION OF COPPER FROM BISMUTH.

It would appear, from experiments made in this laboratory, that the only method yielding satisfactory results in the separation of these two metals in the electrolytic way is that suggested and published by Smith and Frankel[1], *viz.*, the action of the current upon a citrate solution of the metals in the presence of a known amount of potassium cyanide. It is stated upon page 91 of Smith's *Electrochemical Analysis* that copper cannot be separated from bismuth in the presence of free nitric acid, while in the most recent edition (Dritte Auflage) of Classen's *Analyse durch Elektrolyse* we discover statements such as these:

"So scheidet sich durch Einwirkung des Stromes von früher bezeichneter Stärke das Kupfer frei von Wismuth aus" (p. 144); and "Die Trennung gelingt indess aus der freie Saltpetersäure enthaltenden Auflösung" (p. 123). It was this difference of opinion relative to the behavior of these two metals towards the current when in the presence of nitric acid that led us to examine their conduct more carefully, with the results that will appear later.

A copper solution of known strength was first prepared. Two equal portions of it were electrolysed in the presence of twenty cc. of nitric acid (sp. gr. 1.2), and total dilution of 200 cc., with a current that liberated three to four cc. of electrolytic gas per minute. The quantities of copper precipitated were in

a — 0.1342 gm.
b — 0.1340   "

[1] Am. Chem. J., 12, 434.

The required copper equaled 0.1340 gm. It may be remarked that the conditions of experiment in both trials were, so far as the strength of current, total dilution, and the volume of nitric acid were concerned, precisely like those mentioned by Classen as desirable in the separation of copper from associated metals (see *Analyse durch Elektrolyse*, p. 79., 3te Auflage).

A further step in our experimentation consisted in the preparation of a bismuth solution of known strength. It was made up from the nitrate, and contained only as much nitric acid (sp. gr. 1.1) as was found necessary to prevent its decomposition into basic salt upon subsequent dilution with water. Ten cubic centimeters of this solution contained 0.0593 gm. of metallic bismuth.

Experiment 1.—Ten cc. of bismuth nitrate solution (= 0.0593 gms. metallic bismuth), were diluted to 200 cc. with water and electrolysed with a current generating 2.2 cc. of electrolytic gas per minute. The liquid was siphoned off from the metal and the latter washed with water, alcohol, and ether. The precipitated bismuth weighed 0.0587 gm.

Experiment 2.—The conditions were similar to those in experiment 1, but the current gave 2.7 cc. of electrolytic gas per minute. The metal weighed 0.0590 gm.

Experiment 3.—With the conditions as in 1 and 2, and a current that gave 2.1 cc. of electrolytic gas per minute, the deposit of bismuth weighed 0.0593 gm.

Experiment 4.—The conditions were the same as those in 3. The metallic bismuth weighed 0.0595 gm.

The deposit of metal in each of these trials was perfectly adherent and did not exhibit the slightest tendency towards sponginess, which is very likely to be observed when the metal is thrown out of almost any other solution. The metallic bismuth was washed with water, alcohol, and ether. The filtrates remained colorless when treated with ammonium hydroxide and hydrogen sulphide. No deposits were discovered upon the positive pole. It is therefore not too much to say that bismuth can be completely precipitated, even from a nitric acid solution, by the electric current.

What effect would the introduction of stronger nitric acid have

upon the precipitation of this metal? This interrogatory is answered in the following trials:

Experiment 1.—Ten cc. of bismuth nitrate solution (= 0.0593 gm. of metallic bismuth) were diluted to 200 cc. after the addition of 25 cc. of nitric acid of specific gravity 1.2, and then electrolysed with a current liberating 2.4 cc. of electrolytic gas per minute. The deposited bismuth weighed 0.0573 gm. Hydrogen sulphide discolored the filtrate. Bismuth peroxide had also separated upon the positive pole.

Experiment 2.—In this trial the quantity of acid was increased to thirty cc. (sp. gr., 1.2), but the other conditions continued the same. The precipitated metal weighed 0.0425 gm.

Experiment 3.—In this trial we used ten cc. of the bismuth solution (= 0.0593 gm.), five cc. of nitric acid (sp. gr. 1.2,) total dilution 200 cc., and a current that gave three cc. of electrolytic gas per minute. The precipitation extended through the night. The metal deposit weighed 0.0573 gm. The filtrate contained bismuth.

Experiment 4.—The conditions of Exp. 3 were retained here, except that the current gave 3.9 cc. of electrolytic gas per minute. The metal weighed 0.0575 gm. The filtrate contained unprecipitated bismuth.

In these four trials bismuth peroxide was invariably observed on the positive pole. The precipitation of metal was incomplete in the presence of 20–30 cc. of nitric acid, sp. gr. 1.2, and even when a current was used that liberated three to four cc. of electrolytic gas per minute. While the acid, when in considerable quantity, appears to retard the deposition, it fails to do so entirely even when the conditions are such as Classen pronounces satisfactory for the separation of copper from bismuth, etc.

After the above preliminary trials, made to acquaint ourselves with the deportment of the metals when electrolysed separately, we advanced to their separation. Numerous experiments were made. We give the results obtained from a few of these.

Experiment 1.—Ten cc. of copper solution (= 0.1340 gm. of metallic copper) and ten cc. of bismuth solution (= 0.0593 gm. metallic bismuth), with thirty cc. of nitric acid of sp. gr. 1.2 and a total dilution of 200 cc., were electrolysed with a current liber-

ating four cc. of electrolytic gas per minute. The copper deposit weighed 0.1872 gm. The spiral in connection with the positive pole of the battery was thickly covered with bismuth peroxide. The filtrate from the copper did not reveal either metal upon examination. The precipitated copper, after weighing, was dissolved and examined for bismuth, which it contained. The result shows complete precipitation of both metals with the *bismuth appearing at both poles*.

Experiment 2.—Ten cc. of bismuth solution (= 0.0060 gm. metallic bismuth), ten cc. of copper solution (= 0.1340 gm. metallic copper), with twenty cc. of nitric acid of sp. gr. 1.2 and total dilution of 200 cc., gave, when electrolysed with a current generating four cc. of electrolytic gas per minute, a deposit that weighed 0.1387 gm. The filtrate was free from metals. The wire from the positive pole was covered with a black coating that contained bismuth. The metallic copper also contained bismuth.

Experiment 3.—Ten cc. of the copper solution (= 0.1340 gm. copper), ten cc. of bismuth solution (= 0.0006 gm. metallic bismuth), twenty cc. of nitric acid of sp. gr. 1.2, with total dilution of 200 cc., were electrolysed with a current yielding 3.2 cc. of electrolytic gas per minute. The copper deposit weighed 0.1341 gm. The spiral in connection with the positive pole was very distinctly discolored. An examination of the precipitated copper for bismuth was unsatisfactory. This is not surprising when we consider the small amount that had been added. There was, however, no question as to the deposition upon the positive pole, and it is a matter of interest to know that even so small a quantity would present itself at that point. A repetition of the experiment gave a like result.

Experiment 4.—Ten cc. of copper solution (= 0.1340 gm. metallic copper), ten cc. of bismuth solution (= 0.0118 gm. metallic bismuth), twenty cc. of nitric acid, sp. gr. 1.2, with a total dilution of 200 cc., gave, with a current liberating 3–4 cc. of electrolytic gas per minute, a deposit that weighed 0.1432 gm. It contained bismuth. Bismuth was also deposited as oxide upon the positive pole. The filtrate from the metals did not yield a precipitate upon the addition of ammonium hydroxide

and hydrogen sulphide. The precipitation of the two metals was, therefore, complete, but the bismuth presented itself at both poles.

With the above results before us we are compelled to cast our testimony in favor of the statement that these metals cannot be separated electrolytically in a nitric acid solution. We find also that Classen, in describing the manner in which copper can be separated from a nitric acid solution by the current, makes use of the following significant language:

" Bei Gegenwart von Antimon, Arsen, oder *Wismuth gehen Antheile derselben in den Kupferniederschlag über*" (p. 80, *Analyse durch Elektrolyse*).

2. LEAD FROM BISMUTH.

The electrolysis of the nitric acid solution of these metals, it is stated, will lead to their complete separation, the lead being precipitated as dioxide upon the positive pole, while the bismuth separates simultaneously as metal at the negative pole. The results described in the preceding paragraphs, where the separation of copper from bismuth is discussed, would indicate an entirely different behavior. We have never observed any published results, actually obtained by experiment, showing that the separation will work and is in every way satisfactory, therefore our own experience in this direction may be briefly recorded.

A solution of lead nitrate was first prepared. Ten cubic centimeters of the same ($= 0.0996$ gm. metallic lead) were mixed with thirty cc. of nitric acid, sp. gr. 1.2, diluted to 170 cc. with water, and exposed to the action of a current liberating from 2–2.4 cc. of electrolytic gas per minute. The lead dioxide was precipitated upon a rather large platinum dish in connection with the positive pole of the battery. The washing was performed without interrupting the current. The deposit was dried at 110° C. It contained 0.0996 gm. of metallic lead. A second determination conducted in the same manner gave 0.0993 gm. of lead.

We next electrolysed the following solution: Ten cc. lead nitrate ($= 0.0996$ gm. of lead), ten cc. bismuth solution ($= 0.0118$ gm. of bismuth), and thirty cc. nitric acid, of specific

gravity 1.2. The current gave 2.2 cc. of electrolytic gas per minute. The lead dioxide was received upon the platinum dish and the bismuth upon the outside of a large crucible suspended in the solution contained in the dish. The filtrate contained no unprecipitated metal. The lead dioxide weighed 0.1174 gm., instead of 0.1150 gm. (theoretical). The metallic bismuth weighed 0.0017 gm. An examination of the lead dioxide revealed the presence of bismuth. Again, with conditions similar to the preceding, except that the bismuth added equaled 0.0059 gm., the precipitate of lead dioxide weighed 0.1213 gm. instead of 0.1150 gm. (theoretical). It contained bismuth. A third experiment was performed with the result that bismuth was found in the lead dioxide.

3. SEPARATION OF COPPER, LEAD, AND BISMUTH.

A solution containing 0.1340 gm. of metallic copper, 0.0009 gm. of metallic lead. 0.0011 gm. of metallic bismuth, twenty cc. of nitric acid of sp. gr. 1.2, and total dilution of 190 cc., was electrolysed with a current liberating 2–3 cc. of electrolytic gas per minute. The precipitation was complete after twelve hours. The deposit of copper was found to contain bismuth, and the lead was apparently uncontaminated. Upon increasing the quantities of lead and bismuth, the copper and lead dioxide that were precipitated showed bismuth upon examination. The quantities of lead and bismuth were increased in three additional experiments, and in every case the precipitated metallic copper and lead dioxide revealed the presence of the third metal. We have been reliably informed that certain varieties of brass, recently examined, contain bismuth. If these were analyzed in the electrolytic way one might well expect to find the lead dioxide contaminated with bismuth; copper, too, might contain the latter metal.

A further study of the conduct of various metals toward the current, in the presence of nitric acid, is now being made in this laboratory.

* CHEMICAL LABORATORY
OF THE UNIVERSITY OF PENNSYLVANIA.

ABSORPTION BULB FOR SULFUR DETERMINATIONS.

By J. Kenneth Mackenzie.

The bulb of which enclosed is a drawing has been in use in my laboratory for some time, with good results, in the determination of sulfur in iron and steel by evolution as H,S. By its use I avoid the tedious disconnecting of the absorbing bulb from its stand after each analysis. Where fifty or one hundred determinations of sulfur are made daily, the saving of time by the use of this bulb is quite material. The bulb is permanently clamped to an upright rod, screwed down on my work table. When in use it is joined at A, with the usual safety attachment to the flask containing the drillings of the sample under examination. The absorbing liquid, bromin, sodium hydroxid, etc., is introduced through the open end of the bulb at B, and after the complete absorption of the H,S

ABSORPTION TUBE
ILLINOIS STEEL CO. UNION WORKS
Chicago, Feb.,24th,1892. Scale, ½"=1"
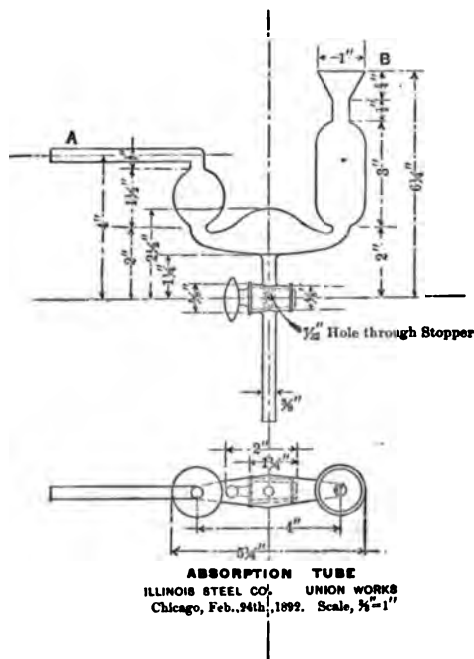
gas has taken place, the stop-cock is opened and the liquid is run into a beaker or porcelain casserole, for subsequent treatment gravimetrically or by titration. The bulb is washed out three times with water introduced at B and run out through the stop-cock as before. With a little care, no difficulty is experienced in keeping the stop-cocks in good order.

AN INVESTIGATION OF COALS·FOR MAKING COKE IN THE SEMET-SOLVAY OVENS, WITH THE RECOVERY OF AMMONIA AND TAR: AND REMARKS ON THE SOURCES OF AMMONIA.[1]

BY J. D. PENNOCK, SYRACUSE, N. Y.

About a year and a half ago, Mr. Morris, an engineer of the Solvay Process Company, was sent to Belgium and France to study the manufacture of coke in the Semet-Solvay ovens, which were in operation at Havre.

With complete plans of construction and a good understanding of the methods of running the ovens, he returned to Syracuse. Work on twelve Semet-Solvey ovens was immediately begun. These ovens, with plant for crushing and washing coal, and the necessary condensers, scrubbers, and concentrator for the recovery of the by-products are nearly finished, and will soon be in operation.

As the work approached completion it became necessary to determine what coal should be used. Accordingly, a chemical investigation of the various bituminous coals was made.

I. INVESTIGATION OF COALS.

The samples of coal taken for analysis were: 1. A sample of Reynoldsville coal that had been exposed to the weather for a year; 2. Reynoldsville coal taken from a car direct from the mine; 3. Morris Run lump coal; 4. Morris Run fine coal; 5. Coal from the Fairmount Coal and Coke Company; 6. A special engine coal from Pardee colliery, Phillipsburg, Pa.; 7. South Fork, Pa., coal; 8. Coal from Laceyville, Ill.; 9. Pittsburg bituminous coal from Ocean mines (gas coal); 10. Steubenville, Ohio, coal; 11. Evansville, Indiana, coal; 12. Coal from the Ohio Coal Company.

Proximate Analysis.

	1.	2.	3.	4.	5.	6.
Water at 90° C.[2]	....	....	....	....	....	....
Volatile	31.14	33.00	17.73	18.12	37.20	23.86
Fixed carbon	64.49	58.07	71.92	71.89	56.68	73.00
Ash	4.37	8.93	10.35	9.99	6.12	3.14
Coke	68-86	67.00	82.27	81.88	61.88	76.80

[1] Trans. A. I. M. E., Montreal Meeting, February, 1893.
[2] Dried before analysis.

	7.	8.	9.	10.	11.	12.
Water at 90° C.		12.20	0.28	0.88	6.73	1.64
Volatile 15.51		41.60	39.09	40.44	38.48	42.275
Fixed carbon 78.60		41.15	57.33	56.60	43.74	45.92
Ash 5.84		5.04	3.30	2.07	11.04	10.16
Coke 84.14		46.19	60.63	58.67	54.78	56.08

1, 2, 3, and 4 all produced a very good coke. 7, on account of low volatile matter, produced a soft coke. The others produced hard cokes, but swelled, some more than others. If all these coals were available at the same price and would make coke of equal quality, then the choice would be of that coal which would yield the most coke per ton of coal. 3 and 4 produced a coke in the laboratory equal to any of the others, and, per hundred of coal, produced more coke; and hence these two coals, on the score of yield of coke, should be chosen.

Impurities in the coal and coke.—Referring to the analysis, it will be seen that 3 and 4 are highest in ash, with one exception—11. But even with this greater amount of ash, there is still a greater amount of carbon in the coke of 3 and 4 than in any of the others, except 6 and 7. The coals from Illinois, Indiana, and Ohio must be withdrawn from the competition on account of their great distance from Syracuse and their very low yield in coke.

Sulfur in the coals and in the coke made from them.—The manufacturer of coke for general metallurgical purposes must well consider the amount of sulfur in the coal used. In coke made from each of the above samples the sulfur was determined in check analyses. The following is the result in comparison with the original sulfur in the coal:

		1.	2.	3.	4.	5.	6.
Sulfur in coal	{	1.21	2.18	0.584	0.83	2.23	0.59
	{	1.12	2.16	0.567	0.82	2.18	0.58
Sulfur in coke		1.07	1.91	0.58	0.73	2.04	0.55

	7.	8.	9.	10.	11.	12.
Sulfur in coal 1.38		2.45	0.72	0.83	1.66	2.32
Sulfur in coke 1.22		2.25	0.68	0.77	1.64	2.25

The coke manufacturer would not hesitate long in making a choice as regards sulfur, supposing the cokes were equal in other respects. Throwing out 6, from which a good coke cannot be

made, then 3, 4, and 9 are the best as regards sulfur.   But 9 is a gas coal, and should not be considered.

Sulfur present in bituminous coal in three forms.—Sulfur occurs in coal combined with iron as pyrites, FeS_2, or with carbon as hydro carbon, or as a fixed sulfate, usually $CaSO_4$.

For the metallurgist, sulfur in the first two forms is specially injurious.   But when the coke is to be used in kilns for the burning of limestone, sulfur in all forms is taken up by the lime, and appears principally in the oxidized form—calcium sulfate. Especially costly is the use of lime containing sulfate of calcium in the manufacture of caustic soda from the carbonate of soda.   In causticizing a ton of carbonate of soda, lime containing two per cent. of sulfate of calcium converts forty-two pounds of the 2240 pounds of carbonate of soda into the less valuable product, sulfate of soda.

In determining the percentage of sulfur present as iron sulfid, I used Dr. Drown's method,[1] with the following result:

Coal.	Sulfur as FeS_2, per cent.
1 Contained 0.616	
3 " 0.12	
6 " 0.09	

It will be seen that the metallic sulfid is present to a great extent in 1, while in 3 and 6 the greater part of the sulfur is present as an organic sulfid and a fixed sulfate.   These analyses are well checked by the analyses of the ash remaining after the carbon of the coal had been burned off.

After fusing with soda in the analysis, and after separating the silica, the acid filtrate, through the intensity of its yellow color, was an excellent indicator of the percentage of iron, and hence of the metallic sulfid originally present in the coal.   No. 1 gave an intensely yellow color, 3 gave only a slightly tinted solution, and 6 was almost colorless.

Analysis of ash from the coals.—No analysis of coal is complete without a careful determination of the constituents of the ash.   The percentage of iron in an ash may be estimated approximately from the color, though not with certainty, as the reddish color may be due to the presence of some other oxid ; for instance,

[1] Trans. A. I. M. E., 8, 569.

manganese. Much iron in a coal produces ferric silicate, which
fuses at a low temperature and forms a slag.

The possible importance, both scientifically and commercially,
of the analysis of an ash, is well illustrated by the case of
Gillespie *vs.* Russel, in Edinburgh (1853), the famous controversy
over the classification of torbanite as a coal or not a coal.[1]

The ash analyses of the coals under consideration are as
follows:

	1.	2.	3.	4.	5.	6.
Color.........	Red.	Red.	Gray.	Gray.	Red.	Gray.
Silica	41.48	40.32	60.95	56.31	33.92	44.28
Al_2O_3	34.68	39.02	35.34	34.80	34.22	45.20
Fe_2O_3	18.75	17.81	1.78	6.56	30.62	1.23
CaO.........	4.38	2.65	1.55	2.83	1.48	5.14
MgO........	0.12	0.07	0.04	0.05	0.11	0.101
SO_3	0.42	0.46	0.28	0.37	0.51	0.78

	7.	8.	9.	10.	11.	12.
Color	Red.	Dark-Red.	Yellow.	Light-Yellow.	Gray.	Reddish-Yellow.
Silica	43.95	28.43	50.45	45.15	51.37	29.48
Al_2O_3	39.54	16.94	38.09	43.96	22.79.	22.90
Fe_2O_3	15.00	38.52	7.37	2.70	10.72	45.56
CaO	1.54	11.22	3.02	3.72	10.67	1.35
MgO	trace	....	....	....	....	....
SO_3.........	0.26	3.79	2.25	4.33	2.48	1.73

8 and 12 were highly charged with pyrites, while 8 and 11 con-
tained layers of gypsum.

[1] *J. Chem. Soc.*, 1874, p. 330; Dana's *Mineralogy*, 1892, pp. 1008, 1009, 1022. A chemist by
the name of Young had a patent for the distillation of coal at low temperatures, with the
idea of obtaining paraffine oil; but on working the process on a commercial scale he
found that torbanite, a shale, is the only substance capable of being employed economi-
cally. Further, if a bituminous mineral or "shale-stone," it was admitted free of duty
into France and Germany.

An important fact in the support of the non-coal nature of the mineral was the absence
of sulfuric acid in the ash. Phillips's analyses (Phillips's *Metallurgy*, 2d. ed., p. 136)
showed that the quantity of sulfuric acid in coals varied from 2.2 to 8.38 per cent.

Professor Anderson, an expert in this case stated that he found in the ash of West
Wemyss coal 2.73 per cent. of sulfuric acid, and that in Methyl coal it was abundant,
while in torbanite he could not find any. Other analyses furnished by experts show
that the ash closely resembles that from bituminous coals, with the exception of the
sulfuric acid. The analyses of the ash may be interesting to some. They are:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	SO_3.	Analyst.
56.09	40.04	3.24	0.34	0.46	none.	T. Anderson.
58.51	34.75	7.00	....	....	none.	T. Stenhouse.
56.70	36.20	3.20	1.30	0 40	traces.	A. W. Hofmann.

Nitrogen in coal.—Having selected the coals desirable for quantity of coke per unit of coal, for physical qualities, for low percentage of ash, and for low percentage of sulfur, it remains to select from these one that will give the most ammonia as a by-product.

Coals vary in nitrogen from 0.6 per cent. in anthracite, to two per cent. in some bituminous coals.

Two methods were used in determining the nitrogen. The first was Varentrapp and Will's, the soda-lime method, which is the combustion in a tube of the coal intimately mixed with soda lime, whereby all the nitrogen in the organic substance is converted into ammonia. This ammonia is absorbed in one-fifth normal sulfuric acid, the excess is titrated with one-fifth normal caustic, and the percentage thus determined.

The other method employed was Kjeldahl's,[1] as applied to the determination of nitrogen in coal. One gm. of the finely divided and powdered coal is placed in a one-fourth liter flask, made of good potash glass, together with one gm. of finely powdered mercury oxid and twenty cc. concentrated sulfuric acid, and heated to boiling for three hours. All varieties of coal, including anthracite, are dissolved in this time. The cooled contents of the flask are then added to a three-fourths liter Erlenmeyer flask, containing a little water; 120 to 140 cc. pure sodium hydrate of 32° B. and 30 cc. of a ten per cent. solution of yellow sodium sulfid are then added; a small piece of zinc is introduced; the flask is fitted to a condenser and flask for holding the condensate, and the distillation is carried on for thirty minutes. The NH_3 is distilled in one-fifth normal sulfuric acid, of which twenty cc. are used, and the excess is titrated with one-fifth normal caustic with phenol-phthalein.

In all cases the Kjeldahl method was used, and in some instances it was checked by the soda-lime method. The determination of the nitrogen resulted as follows:

	1.	2.	3.	4.	5.	6.
Kjeldahl method	1.96	1.62	1.30	1.31	1.96	1.85
Soda-lime method	1.92	1.57	1.40	1.26	1.87	1.78
	7.	8.	9.	10.	11.	12.
Kjeldahl method	1.32	1.02	1.37	1.21	1.12	1.16
Soda-lime method	1.29	....	....	....	....	1.15

[1] *J. Soc. Chem. Ind.*, **5**, 506.

It is generally considered in gas works that the coal highest in nitrogen gives the greatest amount of ammonia. The same would be true in the Semet-Solvay ovens, since the temperature is not high enough to destroy ammonia. Coals 1, 2, 5, and 6 are highest in nitrogen, and, consequently, under equally favorable conditions would give the most ammonia. But they have all been considered undesirable because of their high percentage of sulfur. This leaves the choice, as far as nitrogen is concerned, to 3, 4, 7, and 9. 9 is a gas coal; 7 is higher in sulfur than 3 and 4. 3, 4, and 7 have very nearly the composition of the coal worked successfully at Havre in the Semet-Solvay ovens, as will be seen by the following comparison of analyses: 3, Morris Run, lump; 4, Morris Run, fine; 7, South Fork.

	3.	4.	7.	Havre.
Volatile	17.73	18.11	15.32	16.90
Fixed carbon	71.93	71.89	78.40	65.50
Ash	10.34	9.99	5.62	15.00
Sulfur	0.56	0.83	1.38	....
Nitrogen	1.30	1.30	1.32	....

One cannot see why 3, 4, or 7, should not make good coke at Syracuse in the Semet-Solvay ovens if the Havre coal does, as they are so similar in composition.

Making coke in Syracuse, one would have the advantage in freight by using Morris Run coal, as it is mined in the northern part of Pennsylvania, whereas South Fork coal is mined in the southern part of the state.

Two gms. of each of the first six coals were heated in a tube in a combustion furnace without air, and the ammonia expelled was determined. Two per cent. of lime was added to each, which quantity would not injure the quality of the coke, and might evolve more ammonia. The results of the experiments were:

	Per cent. nitrogen.	Per cent. nitrogen recovered by dry distillation	Per cent. of 100 parts of nitrogen recovered by dry distillation.	Per cent. of nitrogen by dry distillat'n with 2 per ct. lime.	Per cent. of 100 parts nitrogen by dry distillation with 2 per ct. lime.
1.	1.96	0.21	10.6	0.39	19.
2.	1.62	0.21	12.0	0.35	21.
3.	1.30	0.28	21.0	0.39	30.
4.	1.31	0.21	16.0	0.39	29.
5.	1.96	0.29	14.0	0.35	17.
6.	1.85	0.38	20.5	0.42	22.

II. SOURCES OF AMMONIA.

In the manufacture of illuminating gas from coal, the organic nitrogen in the coal is in part converted into ammonia by the action of the evolved hydrogen; a part of the nitrogen remains behind in the coke, and the remainder passes away and is condensed in the tar, or escapes in the gas as free nitrogen. Gas works have furnished, in the past, the crude ammonia liquor from which all the salts of ammonia—carbonate, chlorid, and sulfate—are manufactured. The new source of ammonia will be the same nitrogen of coal, but recovered from gas producers, coke ovens, and blast furnaces. The fixation of the nitrogen of the atmosphere is a problem yet to be solved on the commercial scale. Without considering the many patents granted for this purpose, we will briefly discuss the recovery of ammonia from gas works, gas producers, coke ovens, and blast furnaces.

Ammonia from gas works.—During the year 1886, some 2,150,000 tons of bituminous coal were carbonized in the manufacture of illuminating gas in the United States, yielding 1300 pounds of coke per ton of coal, or 1,397,500 tons of gas coke. If the ammonia were recovered from all of this coal at the average yield of twenty pounds of ammonium sulfate per ton of coal, the production of ammonium sulfate per annum would be 21,500 tons. Probably not more than fifty per cent. of the gas works consuming the above quantity of coal are supplied with the necessary apparatus for obtaining the ammonia from the gas in a sufficiently concentrated liquor (one and one-half to two per cent.) to pay for redistillation. According to Brown's *Directory of Gas Works* in the United States, there were 960 gas companies in 1887. Of these, 510 manufactured from coal. The remainder manufactured from oil or made water-gas, principally by the Lowe process. It is not practicable to recover the ammonia unless the carbonization amounts to 7000 tons per annum.

In selecting a coal for illuminating gas the manufacturer endeavors to procure one high in volatile matter that he may obtain a high yield of gas per ton of coal. Fortunately the bituminous coals rich in volatile matter are usually rich in organic nitrogen, and consequently will yield more ammonia than those containing less volatile matter.

The gas passing from the retort through the hydraulic main and condensers deposits upon the lowering of its temperature tar and ammonia, which are conveyed to the tar well. The gas still contains ammonia which is removed by a scrubber, and goes as a weak ammonia liquor to the cistern. Here the ammonia liquor from the tar well is added. From this cistern the liquor is pumped to the distiller or concentrator, and is made into crude ammonia liquor (seventeen per cent. NH_3) or is converted into sulfate.

The following are analyses of the coal used in two representative gas works of New York State:

	Works (A).	Works (B).	Cannel.
Moisture	0.28	0.88	0.76
Volatile	39.09	38.66	54.20
Fixed carbon	57.33	54.18	38.30
Ash	3.30	6.28	6.74
Coke	60.63	60.46	45.04
Nitrogen	1.37	1.46	1.34
Sulfur	0.72	1.24	0.81

Coal used in works A is from the Ocean mines, Pittsburg, that used in works B is from Westmoreland. Each works uses one per cent. of cannel coal from Kentucky, of which the composition is given above.

The following are the tests of the weak liquors from the above gas works (A), using the Standard scrubber and (B) the Wood scrubber:

	Works (A).			Works (B).		
	Tar Well.	Scrub'er.	To Concentrator.	Tar Well.	Scrubber.	To Concentrator.
Deg. B. at 20° C.,	1.3	2.1	2.	1.2	2.	1.9
Sp. Gr.	1.011	1.015	1.014	1.01	1.014	1.013
Free ammonia,	1.01	2.26	2.02	0.64	1.92	1.87
Fixed "	0.26	0.09	0.14	0.42	0.27	0.26
Total "	1.27	2.35	2.16	1.06	2.19	2.13

Ammonia recovered during the year 1891.

	Works (A).	Works (B).
Coal carbonized, in tons (2000 lbs.)	13.542	12,520
Per cent. nitrogen in coal	1.37	1.45
Ammonium sulfate recovered, lbs	280,252	240,496
Ammonium sulfate per ton coal, lbs.	20.72	19.2

Production of tar.—During the year 1891, works A recovered 187,567 gallons of tar, or fourteen gallons per ton of coal carbon-

ized; works B obtained 168,570 gallons, or 13.4 gallons per ton of coal.

What temperature in the gas retort yields the most ammonia ? Chas T. Lewis' finds that at very low distillation temperature the yield of ammonia is low; that a medium temperature brings out a maximum, and that beyond this higher temperatures result in a slightly diminished production. The following are the different temperatures which are expressed by the yield of gas in cubic feet per ton of coal:

Temperature.	Coal yielding cubic ft. per ton.	Ammonia (NH_3) per ton of coal.	Sulfate $(NH_4)_2SO_4$ per ton coal.
Highest	11,620	7.411 lbs.	28.75 lbs.
Medium	10,162	7.894 "	30.62 "
Lower	9,431	7.504 "	29.11 "
Lowest	7,512	6.391 "	24.79 "

The temperature at which ammonia (NH_3) is decomposed.— When gas retorts are maintained at very high temperatures, there is a possibility of dissociation of the ammonia. This takes place in gas retorts and closed coke ovens at lower temperatures than in gas producers.

Ramsey and Young[2] have investigated the decomposition of ammonia at different temperatures with the following results:

1. In a porcelain tube filled with broken pieces of porcelain:

Temperature. Centigrade.	Per cent. Decomposed.
500	1.57
520	2.53
600	18.28
620	25.28
680	35.01
690	47.71
810–830	69.50

2. In an iron tube filled with broken pieces of porcelain:

Temperature, Centigrade.	Per cent. Decomposed.
507–527	4.15
600 (current very fast)	21.36
600 (current slower)	34.44
628	65.43
676–695	66.57
730	93.38
780	100.

[1] *J. Soc. Chem. Ind.,* 7, 62.
[2] *J. Chem. Soc.,* 45, 88.

3. In a plain glass tube filled with fragments of broken glass tubing.   At 780° C., 1.72 per cent. was decomposed.

4. In a plain glass tube lying in an iron tube.   At 780° C., 0.24 per cent. decomposed.

5. In a glass tube filled with strips of ignited asbestos.   At 520° C., 2.90 per cent. decomposed ; at 780° C., 100 per cent. decomposed.

6. In a plain iron tube (no oxid of iron present).   At 780° C., 100 per cent. decomposed.

It will thus be seen that under the most favorable conditions ammonia begins to decompose at about 500° C.   The nature of the surface of the vessel has a very great influence on the decomposition.

The distribution of the nitrogen of coal in making illuminating gas.—William Foster[1] accounts experimentally for the nitrogen of coal during carbonization in the following way, the coal treated containing 1.73 per cent of nitrogen :

Per cent. nitrogen evolved as NH, in distillation 0.251 ; per cent. nitrogen evolved as cyanogen, 0.027 ; amount of nitrogen in coke furnished by 100 parts coal, 0.842 ; nitrogen from 100 parts of coal unaccounted for, the larger portion of which is presumably present as free nitrogen in the coal gas, 0.610 ; total, 1.730 per cent.   (Watson afterwards found coal tar to contain 1.66 per cent. nitrogen.)

If these figures are further reduced to percentages on 100 parts of nitrogen, their relation to each other becomes more intelligible.

	Per cent.
Nitrogen of coal evolved as ammonia (NH₃)............	14.50
" " " cyanogen	1.56
Nitrogen present in the gas as elementary nitrogen.....	35.26
Nitrogen remaining behind in the coke	48.68
	100.00

Gas producers.—In his address[2] before the Society of Chemical Industry, in 1889, Mr. Ludwig Mond very fully describes his process of obtaining ammonia from gas producers.   Messrs. Rickman and Thompson obtained patents for a process for the

[1] *J. Chem. Soc.*, **43**, 105-110.
[2] *J. Soc. Chem. Ind.*, **8**, 505.

formation of ammonia from the nitrogen of the air. They accomplished their object by passing air and steam through a deep coal fire. Mr. Mond, in his experiments on this process, found that though some ammonia was obtained, there was twice as much ammonia formed when the coal was burned at a moderate temperature by means of steam alone. Though burning with steam alone produced the most ammonia, Mr. Mond soon saw that the process could not be carried out economically on the commercial scale. He therefore devoted himself to the study of so regulating the running of the common gas producer with air and steam as to form and recover the most ammonia.

The gas producer he uses is twelve feet long and six feet wide; steam and air are forced in at the bottom; the ashes drop from the producer into a water lute below; the gas passes off at 450° C. from the center at the top into a rectangular tank, partially filled with water, which is sprayed up, and partially absorbs the ammonia. From here the gas, at a temperature of 100° C., goes to a scrubber filled with perforated bricks, in which the ammonia in the gas is absorbed by sulfuric acid. The resulting sulfate of ammonia liquors are evaporated and made into crystals of sulfate, $(NH_4)_2SO_4$. From this tower the gas, freed of ammonia and at a temperature of 80° C., passes to a second tower filled with wooden blocks, over which cold water flows and condenses the steam. This water, thus heated, is pumped to the top of tower number three, and in turn gives up its heat to the air, which must be heated before it goes to the producer. The gas from the second tower goes to the boilers, where the amount of gas produced from one ton of coal makes steam in quantity equal to seventy-five per cent. of that which one ton of coal would make by hand-firing. The composition of the gas is:

	Per cent.
Carbonic acid	15
Carbonic oxid	10
Hydrogen	23
Hydrocarbons	3
Nitrogen	49

The coal Mr. Mond uses is slack, containing 1.5 per cent. nitrogen and thirty-three per cent. volatile matter.

The yield of ammonia.—In November, 1887, when I visited

the ammonia-soda works at Northwich, England, Mr. Mond was working an experimental producer, and sixteen more were in process of erection. These have now been working successfully for four years. The actual working result is the production of 70.6 pounds of ammonium sulfate, $(NH_4)_2SO_4$, from one ton of coal. This is a high yield,—about three times as much as is obtained from gas works. Three per cent. of tar is produced, but is very thick and is of little commercial value.

The disadvantageous feature of this process of recovering by-products is the enormous volume of gas from which a small amount of ammonia is to be taken. From one ton of coal 160,000 cubic feet of gas (at o° C. and atmospheric pressure) are formed, and this volume is increased by 80,000 cubic feet from the steam admitted. The complete removal of ammonia is only accomplished by the use of acid. In coke ovens and gas works the lowering of temperature and spraying with water is sufficient to remove all the ammonia.

Ammonia from coke ovens.—It was early known that in our method of making coke in the bee-hive oven there was a waste of the valuable by-products, tar and ammonia. Thus far, gas works have been able to supply the wants of this country as regards ammonia; but as the works for making illuminating gas adopt the water-gas plan, and as the agricultural demand for nitrogen in the form of ammonia increases, we shall be forced to reconstruct our ovens to save the ammonia. That time is upon us, and it will not be long before the greater part of our ammonia will be a by-product of the coke oven instead of the gas retort.

England's gas works do not begin to supply the demand for ammonia and a soluble form of nitrogen for agricultural purposes. She imports annually thousands of tons of sodium nitrate from Chili to furnish the nitrogen for her depleted soil.

B. H. Thwaite[1] says 120,000 tons of nitrogen are annually absorbed by the vegetable growth of England, wheat absorbing 37,000, barley 27,000, and oats 57,000 tons.

To compensate for this loss it is necessary to employ 573,000 tons of ammonium sulfate, or purchase from Chili 734,000 tons of sodium nitrate, at a cost of $35,000,000. One-third of the fuel

[1] *Industries.* September 30, 1892.

consumed, if treated rationally, would supply 573,000 tons of ammonium sulfate, and England would be independent of foreign supply.

During the year 1890, in the United States, 16,100,000 tons of bituminous coal were converted to coke. If all this coal were carbonized in Semet-Solvay ovens, the ammonia recovered, at thirteen pounds ammonium sulfate per ton of coal, would be 103,150 tons of sulfate, $(NH_4)_2SO_4$.

Types of ovens.—The different types of open ovens and of closed ovens designed for the recovery of by-products are :

Systems not using by-products.	Using tar-vapors and gases as fuel for heating retorts.	Ovens adapted for recovering by-products and utilizing the gas as fuel.	
		A.	**B.**
Meiler.	Appolt Oven.		Closed Ovens.
Bee-hive Oven.	Coppée Oven.	Admitting air and partial combustion of coal.	
			Knab.
		Jameson's Oven.	Pernolet.
			Simon Carvée.
			Otto-Hoffman.
			Semet-Solvay.

The Meiler.—The meiler, or mound, closely resembles that constructed for producing charcoal from wood. By reason of the desulfurizing action of steam derived from the moisture at the base of the meiler, the coke obtained from it is quite free from sulfur. The ground at the base is often kept damp that moisture may be absorbed. Meiler coke is not as hard as oven coke. The bee-hive oven belongs to this class; it wastes all the by-products, but produces a coke that is unsurpassed in quality.

Appolt oven.—The idea in the construction of the Appolt and Coppée ovens was the utilizing of the gaseous products of the process of coking for heating the retorts. The principal feature of the Appolt oven is that the flames and gases, instead of passing up the flue through the center of the dome, as in the bee-hive, into a main flue, and so to the chimney, pass into flues surrounding and enveloping the inner case of the oven, where sufficient air is admitted to effect perfect combustion. The bottom of the Appolt oven is a movable plate, secured by screw and cross

bar, and thus the coke is readily removed.   The quality of the product is excellent.

Coppée oven.—The Coppée oven resembles Appolt's oven, but the gases and vapors descend from an apperture in the upper part of the oven (by vertical flues heating its sides and supplied with air by means of suitable appertures to insure complete combustion) to flues passing under the bottom, which the flames strongly heat.   A main flue then carries the hot gases to do further duty in heating steam boilers before they finally pass to the chimney.

Jameson's oven.—Particulars of the working of this oven are given by the inventor himself in the *Journal of the Society of Chemical Industry*, **2**, 114, 228, 405, and **4**, 134.

Jameson modifies the bee-hive oven by substituting for the usual floor of the oven on which the coal is carbonized a floor of perforated quarrels, supported on sleeper walls, these perforations being connected with a short vertical flue underneath the floor, from which a pipe passes at right angles towards the hydraulic main, situated some little distance from the ovens.   A branch thus proceeds to this main from each oven in a battery of ovens, and, just before reaching the main, the down pipe from each branch is furnished with a cock for regulating or stopping the exhaust in the oven.   After the removal of the ammonia, the gas is used for producing steam.

The ammonia recovered in the Jameson oven is seven to nine pounds of sulfate per ton of coal.   The Jameson oven was alleged to cost little more than the bee-hive, which it was expected to supersede, inasmuch as by it the by-products were obtained.   But the tar obtained, on account of the low temperature of the ovens, is of inferior quality, and finds no market.   It is lighter than water (having 0.96 specific gravity); contains neither naphthalene nor anthracene; its oils are useless for lubricating or illuminating; the phenols obtained are of little value, and the paraffine extracted is inferior.   In fact, a distillation product is obtained peculiar to the low temperature employed, and without commercial value.

Closed ovens.—M. Carvés was the first to devise and construct a closed oven designed for the recovery of tar and ammonia.

The Simon-Carvés, the Semet-Solvay and the Otto-Hoffman are all closed ovens, in which a purely destructive distillation

takes place. These ovens are the outcome of Knab's oven, an early attempt in this direction which was not successful because a sufficiently high temperature was not obtained. Pernolet worked on similar ideas; but his low temperatures produced an inferior tar. The Simon-Carvée, Semet-Solvay, and Otto-Hoffman are similar in construction, all having regenerators for heating the air before it unites with the gas (from which the ammonia and tar have been recovered) and is returned to the ovens.

The Semet-Solvay oven is thirty feet long, fourteen inches wide on the side of the steam ram (used for forcing out the coke), and fifteen inches on the other, and five feet eight inches high. The advantageous feature of the Semet-Solvay oven is that the wall of the oven is composed of fire-clay retorts, three in number, jointed together one above the other by groove-and-tongue. Through these retorts or flues passes the burning gas, which, through the thin three-inch walls of the retort produces intense heat in the oven. By means of two air-tight doors at each end and these jointed walls the oven is kept perfectly air-tight; and hence a high yield of good coke is obtained. This result is partly due to the narrowness of the oven, which has ten inches less width than the Otto-Hoffman oven (thirty feet long, two feet wide and five feet three inches high).

Quality of the coke from closed ovens.—George Lunge[1] says, "The appearance of the coke generally differs from the bee-hive coke; it usually lacks the brightness and columnar structure of the latter, it is more in the form of large circular blocks, of great strength and density, and less liable to break in filling, in transit, or in tapping."

The distillation products, tar, and ammonia, in the closed ovens, are similar to those from gas retorts; yet the coke from gas retorts is of poor quality, whereas that from closed ovens is good. Watson Smith accounts for the difference in this way: In the closed oven a larger charge of coal (four and a half tons) is used, and is piled up to a considerable height (five or six feet); the thickness of the mass is also considerable (about fifteen to twenty inches). As in the retorts of the gas works, the mass soon attains a coked condition, but being thicker, and hence pene-

[1] Lunge's *Coal Tar and Ammonia*. p. 66.

trated more slowly, it attains a more thoroughly coked or pasty stage than the thinner mass on the gas-retort bottoms can do, before beginning to set again in the incipient stage of the process. But furthermore, in the closed ovens the superincumbent mass of some six feet in height introduces a new and important factor in the production ultimately of a more solid article. The semi-fused fuel is maintained in a soft condition to a late stage by the high temperature of the oven, and becomes thus pressed by its own weight, and sinking down gives on cooling a hard, solid mass. Finally, with so large a charge as four and a half tons, charged under a certain gaseous pressure and with a thickness of material considerably larger in proportion than is found in gas retorts, he believes that during the escape of the tar vapors from the decomposing mass a portion of these must suffer almost complete coking, the pores of the mass becoming thus filled up, whereby the yield of the coke is increased and greater solidity is obtained.

That the prejudice against closed oven coke has been overcome in Germany and France, is shown by the great increase in the number of ovens constructed in the past few years. The records show of the Otto-Hoffman type of ovens the following in Germany :

Year.	Ovens at work.
1884	40
1885	210
1889	605
1892	1205

There are at present 205 ovens of the Semet-Solvay type in operation, and 140 in process of erection.

Yield of coke, ammonia, and tar from closed ovens.—The greatest number of ovens of the Semet-Solvay kind is at Havre, France, where 100 are running successfully. The charge of coal is four tons to an oven, which is drawn every twenty-two hours; the coal used contains only sixteen to seventeen per cent. of volatile matter, and the full theoretical yield of coke is obtained by reason of the tightness of the oven. In actual practice the yield is eighty-one per cent. obtained. As regards ammonia and tar obtained at Havre, where poor coal is used, fourteen pounds of ammonium sulfate and thirty-one pounds of tar is the product from one ton of coal. At the Brunner-Mond Soda Works at Northwich,

England, where a better coal is used, twenty-five to twenty-seven pounds of ammonium sulfate and about eighty-two to eighty-four pounds of tar are obtained from one ton of coal.

Benzene from closed coke ovens.—According to Lunge[1] one ton of good bituminous coal yields about 11,000 cubic feet of gas containing 11.7 kilos or 25.7 pounds of benzene. By reducing the temperature of this gas to —70° C. this benzene is precipitated out of the gas. Of course the removal of the benzene would injure the illuminating qualities of the gas, and it would not be advisable to remove the benzene from such a gas.

The best result thus far obtained in removing benzene from coke-oven gas is seventeen pounds, or about sixty-nine per cent. of the theoretical amount.

Ammonia from blast furnaces.—The least developed source of ammonia recovered from the nitrogen of coal is blast furnace gases. Of course this is only practicable where raw coal is used as fuel, the upper part of the furnace becoming a coking chamber. The difficulty here is the removal of a small amount of ammonia from a very large volume of gas.

Lunge[2] states that at 260° C. the gas containing this small amount of ammonia occupies a volume of 230,000 cubic feet, or thirteen times that from a ton of coal burned in a retort. There is a further objection to attempts at the removal of ammonia from these gases, namely the thermal loss due to condensation and cooling, which amounts to 7.4 per cent. of the sum of the sensible heat of the gases.[3]

In the analytical work of this paper, I have been assisted by Mr. W. O. Wood.

DETERMINATION OF PHOSPHORUS IN IRONS AND STEELS.[4]

BY ADOLPHE CARNOT.

It is known that steels and irons of good quality can contain merely a very small proportion of phosphorus, and that a few ten-thousandths of that element suffice to modify greatly the prop-

[1] Lunge's *Coal Tar and Ammonia*, p. 31.
[2] Lunge's *Coal Tar and Ammonia*, p. 86.
[3] R. H. Thwaite, *Industries*, September, 1892.
[4] Chem. News, from *Comptes Rendus*, 116, 105.

erties of the metal.   Hence the greatest importance is attached
to an exact determination of the proportion of phosphorus.

Numerous methods have been proposed and give in different
laboratories results which are often little accordant.   The method
which I am about to describe, founded, like most others, on the use
of ammonium molybdate, yields with less trouble more regular
and more trustworthy results.

It differs from them (1) by the method of separation (and of
determination) of the silicon, which is affected by means of sul-
furic acid; (2) by the process for destroying the compounds of
carbon in which chromic acid is employed ; (3) by the nature of
the final compound which is not magnesium pyrophosphate con-
taining 27.928 per cent. of phosphorus, but dried ammonium
phospho-molybdate, which when obtained by a second precipi-
tation under identical conditions presents a constant composition.
It only contains 1.628 per cent. of phosphorus, *i. e.*, seventeen
times less than the pyrophosphate.   Hence there is much
greater accuracy in the determination.

We operate upon a portion of five gms. for irons, steels, and pure
cast metal,—one gm. or even 0.5 gm. being sufficient for phos-
phoriferous cast metals.   The metal is treated with forty cc. of
pure nitric acid in a large porcelain capsule, which is covered at
once with an inverted funnel in order to avoid the projection of
liquid drops.   When the effervescence is at an end we heat gently
to complete the action, and wash out the funnel with a little
water, which is then received in the capsule.   We add, while
stirring up the liquid with a glass rod, ten cc. of concentrated
sulfuric acid (two cc. per gm. of metal).   There is produced
a bulky pulp which redissolves on stirring and heating.   We
evaporate gently, either over a small rose burner, stirring con-
stantly for a quarter of an hour, or leaving it on the sand bath
for a longer time.   The mass soon becomes pasty and then dry,
becoming reduced to grains which are easily crushed with the
stirring rod.

It is placed on the stove and kept for two hours at a tempera-
ture of 120° to 125°, so as entirely to expel the nitric acid and ren-
der the silica throughout the mass quite insoluble.   It is then re-
dissolved in fifty cc. of boiling water and washed on a filter with

an equal quantity of water, receiving the liquid in a liter flask.

The silica remains on the filter. It is generally colored black or gray by graphite, and may be mixed with manganese peroxid. The latter is dissolved in another flask in a little concentrated hydrochloric acid and washed with hot water. We ignite to burn off the graphite and weigh the silica, which will have become white. This weight, multiplied by the coefficient 0.4667, gives an exact determination of the silicon, as in Drown and Shimer's method.

The filtrate contains the organic compounds derived from the transformation of the iron carbid under the action of the acids which might hinder the precipitation of the phosphoric acid. In order to burn the organic matter we add about one gm. of chromic acid and heat for half an hour to the temperature of ebullition. This operation has the advantage of certainly restoring to the state of orthophosphoric acid any trace of pyrophosphoric acid which may have been formed during the evaporation to dryness.

We then pour into the liquid sixty to eighty cc. of a molybdic solution at five per cent., prepared as usual, and keep it at 100° for two or three hours, the time necessary for a complete precipitation. It is allowed to settle and cool, and the liquid is decanted upon a filter and the deposit is washed in the flask with lukewarm water containing one-twentieth of its volume of molybdic solution until the washing water is only colored a very slight rose by the addition of ammonium sulphocyanid, *i. e.*, until it contains merely negligible traces of iron.

We then dissolve the precipitate in the flask with thirty cc. of ammonia diluted with an equal volume of hot water, and placing the funnel with the filter upon a small flask, holding 150 cc., into which the acid liquid has been decanted, we introduce the ammoniacal solution. We wash the flask and the filter with fifty cc. of boiling water, slightly ammoniacal, making use of the filter pump.

The filter may retain small quantities of ferric hydrate and phosphate, which are redissolved in a few drops of hot, dilute nitric acid, which are subsequently added to the acid liquid.

The ammoniacal solution, filtered and cooled, is gradually neutralized by nitric acid, not raising the temperature above 40°.

When a yellow precipitate begins to appear, which does not re-dissolve on stirring, we add as a surplus three cc. of pure nitric acid and the small quantity of dilute acid which has served to wash the filter.

It is left for two hours at a temperature of about 40°, for the precipitation of the ammonium molybdate. The liquid is then decanted upon a tared filter and replaced by water acidified with one per cent. of nitric acid. After two or three wash-ings the precipitate is placed upon the filter, washed with a little distilled water by means of the pump, dried at 100° in the stove, and weighed in a small special bottle with a wide mouth so that the filter may be introduced without breaking.

By this second precipitation of ammonium phospho-molybdate in conditions of temperature and acidity perfectly defined, we obtain a product of constant composition free from iron and from excess of molybdic acid, which is not regularly effected with the first precipitation. The weight of the phosphorus present is obtained by multiplying the weight of the dried precipitate by the coefficient 0.01628.

RAPID QUALITATIVE EXAMINATION OF MINERAL SUBSTANCES.[1]

BY ALFRED J. MOSES. PH. D., AND J. S. C. WELLS. PH. D.

This scheme is designed for the rapid determination of the essential constituents of minerals, and also for the preliminary examination which should precede separation into groups and thorough qualitative analysis. Preference is given to dry or blow-pipe tests, but where, as in silicates, these have proved unreliable, a simple wet method has been introduced.

The intention has been to outline a simple order of work and to give with this confirmatory tests in sufficient detail to enable any one at all familiar with analytical work to be sure of results, without having to refer at each step to some manual of tests.

The tests are given in large type, the confirmatory tests and notes in smaller type. A few abbreviations, such as S. Ph. for salt of phosphorus, soda for sodic carbonate, O. F. and R. F. for

oxidizing and reducing flames, are used.   The general outline
is as follows:

I. Substances yielding noticeable coatings:
    A. By gentle oxidation upon blackened plaster.
    B. By reduction with soda upon charcoal.
    C. By the aid of bismuth flux upon plaster.

II. Substances contained in the mass resulting from the fusion
       with soda on charcoal.
    A. Magnetic particles.
    B. Elements combined with the soda.

III. Substances which are not driven from a salt of phosphorus
       bead by reduction.
    A. The bead in O. F. (cold) is colorless, or very faint yellow.
    B. The bead in O. F. (cold) is yellow or greenish yellow.
    C. The bead in O. F. (cold) is violet.
    D. The bead in O. F. (cold) is green.
    E. The bead in O. F. (cold) is blue.
    F. The saturated bead is either white and opaque cold or
       contains an appreciable amount of insoluble matter.

IV. Special tests for substances not included in I, II, or III.

I. SUBSTANCES YIELDING SUBLIMATES ON PLASTER
OR CHARCOAL.

Test A.—Heat a portion gently with O. F. upon a plaster
    tablet which has been blackened in the lamp flame.[1]

Sb.—White pulverulent volatile coat.

> The compound often continues to form in dense white fumes after
> cessation of blast. The coating disappears before R. F. tingeing it
> a pale yellow green, or if scraped together, dissolved in S. Ph.,
> and just fused on coal in contact with tin it will form a gray or black
> opaque bead.

Confirmation Sb.—If the coating be scraped off and dissolved in tartaric acid + HCl,
and the solution placed in a platinum capsule with a piece of zinc, antimony, if present,
will give a black adherent stain.

Confirmed by washing the stain with water, then dissolving it in a few drops of hot
tartaric acid plus a drop or two of HCl; on adding H_2S an orange precipitate = Sb.

[1] Charcoal may be used, but as plaster condenses the oxids closer to the assay, the
volatile coatings of arsenic and antimony upon it are much thicker and more noticeable.
See Moses, *School of Mines Quarterly,* 10, 321.

As.—White very volatile crystalline coat.

> The coat disappears before R. F., tingeing it pale blue and evolving a characteristic garlic odor.

> There may also be formed non-volatile coatings of Sn or Zn near the assay, yellow hot, and white cold; yellow coatings of Pb or Bi; crystalline yellow and white coating of Mo; brick red to crimson coating and horseradish odor of Se and deep brown coatings of Cd and Te. All of these will be detected with greater certainty by later tests.

Confirmation **As.**—The coating may be dissolved in solution of KOH, placed in a test tube, a small piece of sodium amalgam added, and the tube covered with a piece of filter paper moistened with a slightly acid solution of $AgNO_3$. The paper will be stained black by the AsH_3 evolved.

Test B.—Heat a portion gently with the R. F. on charcoal, and note the results; then add a spoonful of soda and a little borax, and heat strongly with the R. F. for three or four minutes. Preserve the fused mass for subsequent examination by II.

As.—Garlic odor and a faint, white, volatile coat.

Cd.—Dark brown volatile coat, sometimes shading to greenish yellow and usually surrounded by a variegated coloration resembling the colors of peacock feathers.

Confirmation **Cd.**—The coat forms at first heating, and if fused with $Na_2S_2O_3$ will form a bright yellow (CdS) mass.

Zn.—White, not easily volatile coat, yellow when hot.

Sn.—White non-volatile coat, close to assay, and usually small in amount.

> White coats may form from Pb, Bi, or alkalis, yellow coats from Pb or Bi, brown or red coats from Cu or Mo, and the ash of the coal may be white or red.

> If any coat forms, examine it for Zn and Sn by moistening it with cobalt solution and blowing a strong blue flame on the substance. The coatings from other elements will not prevent the cobalt coloration.

Confirmation **Zn and Sn.**—The zinc coat is made bright yellowish green by moistening with dilute cobalt nitrate and igniting.

The tin coat becomes bluish green on ignition with dilute cobalt nitrate.

Test C.—Mix a portion of the substance with more than an equal volume of bismuth flux[1] and heat gently upon a plaster tablet with the oxidizing flame.

[1]Formed by grinding together 1 pt. KI, 1 pt. $KHSO_4$, 2 pts. S. See Moses, *School of Mines Quarterly*, 10, 324.

Pb.—Chrome-yellow coat, darker hot, often covers the entire tablet.

Sn.—Brownish orange coat.

Confirmations *Test C* (general).—If the test with bismuth flux is made upon charcoal, there would result

Pb.—Greenish yellow coat, brown near the assay.

As, Sb, Hg, Bi.—Very faint, volatile, yellow or reddish coat at a distance.

Sn.—By strong heat a white coat of the oxid.

Bi.—Bright red band, with sometimes an inner fringe of yellow.

As.—Reddish orange and yellow coat, darker hot.

Confirmation As.—The coat becomes lemon-yellow when moistened with $(NH_4)_2S$.

Sb.—Orange to peach-red coat, very dark when hot.

Confirmation Sb.—The coat becomes orange when moistened with $(NH_4)_2S$.

Hg.—Gently heated, bright yellow and scarlet coat, very volatile, becomes all scarlet on standing; but if quickly heated, the coat formed is pale yellow and black.

Confirmation Hg.—If the substance is heated gently in a closed tube or matrass with dry soda or litharge, a mirror-like sublimate will form which may be collected into little globules of Hg, by rubbing with a match end.

Bi.—Bright scarlet coat surrounded by chocolate-brown with sometimes a reddish fringe.

Large amounts of certain other elements may yield colored sublimates, and on smoked plaster certain white sublimates are obtainable; in all cases the elements are detected with greater certainty by other tests; but for convenience they are here summarized: Se, reddish brown; Te, purplish brown, with deep brown border; Mo, deep ultramarine blue; Cu, Cd, Zn, white (on smoked plaster).

Confirmation Bi.—The coat is turned orange-yellow, then cherry-red, by fumes of NH_3, which may be produced convieneently by heating a few crystals of S. Ph. on the assay.

II. SUBSTANCES' CONTAINED IN THE MASS RESULTING FROM THE FUSION WITH SODA ON COAL.

Crush and pulverize, collect any magnetic particles with the magnet; place the balance of the powder upon a bright silver surface, moisten with water and let stand.

Test A.—Dissolve some of the magnetic particles in a borax bead with the O. F. Try also effect of R. F.

Fe.—The bead is: O. F. hot, yellow to red; O. F. cold, colorless to yellow; R. F. cold, bottle-green.

Confirmation Fe.—The magnetic particles yield with HNO_3, a brown solution from which, after evaporating excess of acid, $K_4Fe(CN)_6$ throws down a blue precipitate.

'There may be contained in the soda also metallic particles or buttons, which may be roughly recognized by color and tenacity as follows: Brittle—Sb, white; Bi, reddish white. Malleable—Ag, silver-white: Pb, gray; Au, yellow; Cu, red.

Ni.—The bead is: O. F. hot, intense violet; O. F. cold, pale brown; R. F. cold, colorless.

Confirmation Ni.=If the excess of acid be driven off by evaporation, KCN added in excess, and the solution then made strongly alkaline with KOH, two or three drops of pure bromin will give a black precipitate of $Ni_2(OH)_6$. Should the addition of the bromin make the solution neutral or acid, more KOH must be added until reaction becomes strongly alkaline.

Co.—The bead is: O. F. and R. F. hot or cold, a deep pure smalt blue; if greenish when hot, probably Fe or Ni is also there.

Confirmation Co.—The magnetic particles yield with HNO_3, a rose-red solution which becomes blue on evaporation.

Test B.—The bright silver is stained black or dark brown.

Unless the horseradish odor of Se or the brown coatings of Se and Te with bismuth flux have been already obtained, this stain will prove sulfur.

S.—The soda fusion will evolve H_2S when moistened with HCl.

To distinguish sulfid from sulfate, fuse a little of the original substance with soda in a porcelain crucible, put a piece of bright silver in the crucible and add a little water. A black stain equals sulfid. Remove silver, dissolve fusion in hot water and filter, acidify filtrate with HCl. Evolution of H_2S if sulfid is present. Add $BaCl_2$, white precipitate equals sulfate.

· Confirmation S.—By holding in the gas a piece of filter paper moistened with a drop or two of lead acetate (test is made more sensitive by adding a drop of ammonia to the acetate), the paper will be stained black.

The soda fusion dissolved in water will give a brownish black precipitate on addition of a solution of lead acetate in KOH.

The soda fusion moistened with water on a watch glass will yield a magnificent purple red color on addition of sodium nitro prussid.

Se.—Characteristic disagreeable horseradish odor during fusion.

Te.—The quite cold soda fusion added to hot water produces a purple red solution.

Confirmation Te.—If a little of the original substance is dropped into boiling concentrated H_2SO_4 a deep color is produced; this disappears on further heating.

III. EXAMINATION IN SALT OF PHOSPHORUS BEAD.[1]

Dissolve substance in salt of phosphorus in O. F. so long as bead remains clear on cooling. Treat then for three or four minutes in a strong R. F. to remove volatile compounds.

[1]If any of I and II have been found except Co, Ni, and Fe it is better to submit the substance to a slow heating in the O. F. and R. F. Turn the material occasionally, and if it agglomerates, re-pulverize and again roast. Continue till no noticeable fumes are given off.

Note the color hot and cold, then reoxidize and note colors hot and cold.

Test A.—If the bead in O. F. cold is colorless or very faint yellow, reduce it on coal with tin, and if then colored, pulverize and dissolve in hot dilute ($1:4$) HCl with addition of a little metallic tin.

Fe.—The reduced bead is colorless.

Confirmation Fe.—The bead in its previous treatment should have been O. F. hot, yellow to red ; O. F. cold, colorless ; R. F. cold, bottle-green.

Tl.—The reduced bead is violet, the solution is violet and turbid.

Mo.—The reduced bead is green, the solution is dark brown.

Confirmation Mo.—Heat a little of the substance in Pt foil with a few drops of conc. HNO_3; heat until excess of HNO_3 has all volatilized, then add a few drops of strong H_2SO_4 and heat until copious fumes are evolved ; cool, and breathe upon the cooled mass, an ultramarine blue = Mo.

Heat substance on charcoal in O. F. ; scrape off coating obtained, dissolve in NH_4OH and add to an excess of HNO_3 ; then add one drop of dilute solution of Na_2HPO_4, a yellow ppt. = Mo. (As must not be present).

W.—The reduced bead is green, the solution is deep blue.

Test B.—If the bead in O, F., cold, is colored yellow or greenish yellow, treat it in a strong reducing flame.

U.—In R. F. the bead will be dull green hot, fine green cold.

Confirmation U.—Make a Na_2CO_3 fusion, dissolve in HCl or H_2SO_4, add a few drops of H_2S water, and if it gives any precipitate, add it in excess and filter ; to filtrate add a few drops of HNO_3 and boil, then add NH_4OH to alkaline reaction, filter, wash precipitate with ammonia water, and then treat precipitate with concentrated solution of $(NH_4)_2CO_3 + NH_4OH$, filter and acidify filtrate with HCl, and add $K_4Fe(CN)_6$. Brown ppt. = U.

V.—In R. F. the bead will be brownish hot, fine green cold.

Confirmation V.—Fuse substance with Na_2CO_3 in O. F. and dissolve fusion in a few drops of dilute H_2SO_4 or HCl, add a piece of zinc and warm ; blue color changing to green and finally violet = V.

Or, shake acid solution with ether and hydrogen dioxid and if V is present, the aqueous solution becomes red.

Ni.[1]—In R. F. the bead will be reddish hot, yellow cold.

Confirmation Ni.—The hot bead in O. F. will be intense violet.

[1]If the absence of Ni is not proved, or Co obscures the tests, dissolve the substance in borax on coal to saturation, and treat for five minutes in hot R. F.

If a visible button results, separate it from the borax, and treat with S. Ph. in the O. F., replacing the S. Ph. when a color is obtained.

If no visible button results, add either a small gold button or a few grains of test lead. Continue the reduction, and if lead has been used, scorify the button with frequently

Test C.—If the bead in O. F., cold, is colored violet, touch the
     bead while hot to a crystal of niter.

Mn.—The bead is made deep permanganate color.

Test D.—If the bead in O. F., cold, is colored green, the sub-
     stance is fused with a paste of soda on platinum wire in the
     O. F., with the addition of niter or $KClO_3$.

Cr.—A bright chrome-yellow.

     There may be a green bead from admixture of a blue and a yellow. If
          Cr is not proved, examine in such a case by tests B and E with
          unusual care.

   Confirmation Cr.—If the soda bead is dissolved in water, filtered, if necessary, acidi-
fied with acetic acid and a drop or two of plumbic acetate added, a yellow precipitate
will be formed.

   By dissolving the soda bead in water, acidifying with H_2SO_4 and adding it to a very
dilute solution of hydrogen dioxid covered with a layer of ether, on closing the test tube
with the thumb and inverting it two or three times the ether will become blue.

Test E.—If the bead in O. F., cold, is colored blue.

Co.—The bead is deep blue, hot and cold, in both flames.

Cu.—The bead is green, hot, greenish blue, cold, and on reduc-
     tion becomes opaque brownish red.

   Confirmation Cu.—Boil a few grains of the substance with strong HNO_3, add excess of
NH_4OH, deep blue solution = Cu. Acidify blue solution with acetic acid and add
$K_4Fe (CN)_6$. Reddish brown precipitate = Cu.

Test F.[1]—If the saturated bead in O. F. is white and opaque,
     when cold, or contains an appreciable amount of insoluble
     material.

     This result may be due to one or more of Ba, Ca, Sr, Mg, Al, SiO_2, Sn,
          Ti, and there may be revealed also Li, K, Na, Fe, etc.

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changed boracic acid to small size, stopping the instant the boracic acid is colored, by
Co, Ni, or Cu, blue, yellow or red respectively.

   Complete the removal of lead by O. F. on coal and treat as below.

   Treat the gold alloy, or the residual button from the lead alloy, on coal, with fre-
quently changed S. Ph. in strong O. F.

   The metals which have united with the gold or lead will be successively oxidized,
and their oxids will color the S. Ph. in the following order :

     Co.—Blue, hot ; blue, cold. May stay in the slag.

     Ni.—Brown, hot ; yellow, cold. May give green with Co or Cu.

     Cu.—Green, hot ; blue cold. Made opaque red by Sn and R. F.

   The slag should contain the more easily oxidizable metals, and be free from Cu, Ni,
and Ag. Test a portion with S. Ph. and Sn to prove absence of Cu. If present it must be
removed by further reduction with Pb. Pulverize the slags and dissolve a portion in
S. Ph. and examine by III.

   [1]In addition to SiO_2 we have here the natural alumina and aluminates, oxids of tin,
oxid of titanium, etc. The usual reactions for Ba, Ca, Sr, Mg, Al, also fail in most
natural silicates, especially where the substance is dark colored or fusible.

SiO₂.—The insoluble material is in the form of a translucent cloud, jelly-like mass, or skeleton form of the original material added.

Confirmation SiO₂.—Mix the dry substance with a little dry fluorid (free from SiO₂), place in a dry test tube and add H₂SO₄ (conc.) and heat gently, hold in fumes given off a drop of water in loop of platinum wire; SiO₂ will be separated on coming in contact with the water, forming a jelly-like mass.

(a) Treat the finely pulverized mineral with Zn and HCl in contact with platinum.[1] Dissolve any reduced metal in HCl and test with HgCl₂.

Sn.—White or gray precipitate.

(b) Moisten the roasted substance with cobalt solution, and heat strongly.

Mg.—Pale pink or flesh color. Violet if present as either arsenate or phosphate.

Al.—Beautiful blue, infusible.

SiO₂.—Faint blue.

There may also be blues from fusible silicates, phosphates, and borates, greens from oxids of Zn, Sn, Ti, Sb, violet from Zr, and various indefinite browns and grays.

(c) Moisten the flattened end of a clean platinum wire with dilute hydrochloric acid, dip it in the roasted substance, and heat strongly at the tip of the blue flame, and gently near the wick. Re-moisten with the acid frequently.

Ba.—Yellowish green flame, bluish green through green glass.

Ca.—Yellowish red (brick red) flame, green through green glass.

Sr.—Scarlet red flame, faint yellow through green glass.

This test may also show:

Li.—Carmine red flame, invisible through green glass.

K.—Rose violet flame, reddish violet through blue glass.

Na.—Orange yellow flame, invisible through blue glass.

There may also be produced Cu azure blue and emerald green; Se and As pale blue; Mo, Sb, Te, pale green.

When tests (b) and (c) fail to give satisfactory results, proceed as follows:

(d) Remove the volatile constituents as thoroughly as possible by roasting, then heat gently in a platinum capsule, with

[1]See Wells, *School of Mines Quarterly.*

about twice the quantity of NH_4F, and a few drops of concentrated H_2SO_4 as long as fumes are given off; add a little more NH_4F and H_2SO_4, and heat again in the same way. To the residue in the capsule, add two or three parts of $KHSO_4$, and a few drops of H_2SO_4, and heat ten or fifteen minutes at a temperature just sufficient to slowly drive off fumes of SO_3. Heat until no more SO_3 is given off, then add a few drops of concentrated H_2SO_4, and heat again for a minute. When fusion is quite cold, dissolve in cold water and filter.

Residue a.—Boil with strong solution of $(NH_4)_2SO_4$ and filter.

Residue b.—Moisten with concentrated HCl and try coloration of flame.

Ba.—Yellowish green flame.

Sr.—Scarlet flame.

Confirmation Ba and Sr.—Or may test residue b as follows : Fuse with two to three pts. of soda in a platinum capsule ; treat fusion with boiling water, filter, reject filtrate, dissolve residue in acetic acid, add a few drops H_2S water, if it gives any precipitate, saturate with H_2S and filter, and to filtrate add $K_2Cr_2O_7$. Ba = yellow precipitate. Filter and to filtrate add $CaSO_4$ warm and let stand. Sr = white precipitate.

Filtrate b.—Add a few drops of H_2S water; if any precipitate forms, saturate with H_2S and filter, and to filtrate add NH_4OH and $(NH_4)_2C_2O_4$.

Ca.—A white precipitate.

Filtrate a.—Divide into four parts and test as follows:

- (1) Add a piece of Zn or Sn and a little HCl, and heat.

Tl.—A violet or blue solution.

Confirmations Tl.—Nearly neutralize solution, and then add $Na_2S_2O_3$, and boil white ppt. = Tl.

Or, make solution slightly alkaline, and then acidify slightly with HCl, and add Na_2HPO_4. White ppt. = Tl.

(2) Add excess of KOH' or NaOH, boil and filter, and to filtrate add excess of NH_4Cl and boil.

Al.—White precipitate.

Dissolve ppt. produced by the KOH or NaOH, in HCl, and add $K_4Fe(CN)_6$.

Fe.—Blue precipitate.

[1]Be sure that the KOH or NaOH is free from Al and SiO_2; they are common impurities.

(3) Add $NH_4OH + (NH_4)_2S$ in slight excess and filter; to filtrate add Na_2HPO_4.

Mg.—White crystalline precipitate.

Confirmation Mg.—If phosphates were present this test would not be reliable for Mg. In such cases test a few drops of the solution with H_2S; if it causes any precipitate, saturate the whole of the solution with it, filter, and to filtrate add a few drops of HNO_3, and boil (to oxidize FeO), nearly neutralize with solution of Na_2CO_3 (if iron is not present, add a few drops of Fe_2Cl_6, enough to give a red precipitate with the sodium acetate), dilute and add excess of sodium acetate, and boil, filter, and to filtrate add $NH_4OH +$ $(NH_4)_2S$, filter, to filtrate add Na_2HPO_4. White crystalline precipitate = Mg.

(4) Add $BaCl_2$ as long as it gives a precipitate, then $Ba(OH)_2$ to alkaline reaction, boil, filter, and to filtrate add $(NH_4)_2CO_3$ and NH_4OH and heat, filter; evaporate filtrate to dryness and ignite to drive out NH_4 salts. Test residue in flame for K and Na; dissolve residue in a few drops of water (filtering if necessary) and then add $H_2PtCl_6(PtCl_4)$ and alcohol.

K.—Yellow cryst. precipitate.

Confirmations Na, K.—Mix 1 part of the silicate with 5-6 parts of $CaCO_3$ (precipitated) and 1 part of NH_4Cl, heat to redness in platinum capsule for thirty minutes (apply heat gently at first), digest sintered mass in hot water, and filter; to filtrate add $(NH_4)_2CO_3$ and NH_4OH, heat and filter, evaporate filtrate to dryness and ignite gently until all ammonia salts are driven off, then determine Na and K as above.

IV. SPECIAL TESTS FOR SUBSTANCES NOT INCLUDED IN I, II, III.

Test A.—Cupellation for silver and gold. Fuse one spoonful of roasted substance on charcoal with one volume of borax glass, and one to two volumes of test lead in R. F. for about two minutes. Remove button and scorify it in R. F. with fresh borax, then place button on cupel and blow O. F. across it, using as strong blast and as little flame as are consistent with keeping the button melted.

If the litharge is dark, or if the button freezes before brightening, or if it brightens but is not spherical, rescorify it on coal with borax, add more test lead, and again cupel until there remains:

Ag.—A bright white spherical button unaltered by further blowing.

Confirmation Ag.—Dissolve in a drop of HNO_3, and add a drop of HCl, producing a white curd-like precipitate.

Au.—A residue, after boiling the button in HNO_3, which becomes golden yellow on ignition.

Test B.—Heat substance in matrass with potassium bisulfate.

N_2O_4.—Reddish brown vapor with characteristic odor.

Confirmation N_2O_4.—Heat in test tube with a small piece of copper or copper filings, and conc. H_2SO_4, red or brown fumes = nitrates or nitrites.

Br.—Reddish brown, choking vapor.

Cl.—Yellowish green vapor.

I.—Violet choking vapor.

Confirmations Br, Cl, I.—Saturate a salt of phosphorus bead with CuO, add substance, and treat in O. F. Br, azure blue and emerald green flame. Cl, pure azure blue flame. I, emerald green flame.

Fuse with Na_2CO_3, pulverize and mix with MnO_2, and add a few drops of conc. H_2SO_4, and heat. Cl, yellowish green gas that bleaches vegetable colors. Br, red fumes.

Fuse with Na_2CO_3, dissolve in water, make slightly acid with H_2SO_4, and add $Fe_2(SO_4)_3$ (ferric alum may be used), and boil ; I, violet fumes (turn starch paper blue).

F.—The glass of the matrass is corroded, and if SiO_2 is present a film of SiO_2 is often deposited.

There may also be evolved various colorless gases, such as SO_2, H_2S, CO_2, etc. which are more safely recognized by other tests.

Confirmation F.—If the substance be mixed with silica and then heated with concentrated sulfuric acid, and the fumes caught on a drop of water held in a loop of platinum wire, gelatinous silica will form in the water.

Test C.—Heat the substance gently with water to remove air bubbles, and then with dilute hydrochloric acid.

CO_2.—Effervescence continuing after heat is removed.

H_2S, Cl, and H are sometimes evolved, but usually the odor will distinguish these.

Confirmation CO_2.—If the gas is passed into lime water, a white cloud and ppt. will be produced.

Test D.—Place a piece of Mg wire in a closed tube, and cover the wire with a mixture of soda and the substance. Heat till the mass takes fire, cool and add water.

P.—Evolution of phosphuretted hydrogen.

Confirmations P.—Fuse a little of the substance (previously roasted if it contains As), with two or three pts. Na_2CO_3 and 1 $NaNO_3$, dissolve in HNO_3, and add excess of $(NH_4)_2$ MoO_4, yellow ppt. = P_2O_5. In presence of SiO_2 it is well to confirm this ppt. by dissolving it in dilute NH_4OH, allowing it to stand for half an hour and filtering off any SiO_2 that separates, then to filtrate adding magnesia mixture. $(MgCl_2 + NH_4Cl + NH_4OH)$ and white ppt. = P_2O_5.)

Or, take nitric acid solution of fusion, make alkaline with NH_4OH; then acidify with acetic acid and add drop or two of Fe_2Cl_6, yellow white ppt. = P_2O_5.

Test E.—Make a paste of four parts $KHSO_4$, one part CaF_2, water and substance. Treat at tip of blue flame.

B.—Just after water is driven off there will be a bright green flame.

Confirmation B.—Heat some of the substance gently on platinum wire, then add a drop of concentrated H_2SO_4, heat very gently again, just enough to drive off excess of H_2SO_4, dip in glycerin, hold in flame until glycerin begins to burn, remove from flame, and the mass will continue burning with a green flame.

NOTES ON EMMERTON'S METHOD FOR THE DETERMINATION OF PHOSPHORUS.[1]

BY H. C. BABBITT.

The Effect of Arsenic.—A question involving the temperature of precipitation of ammonium phospho-molybdate, which was brought to my attention some time ago, led to the following experiment :[2]

A known quantity of arsenic was added to a steel solution, and the yellow salt was precipitated at varying temperatures, with the following results:

Temperature, deg. C 85   70   60   50   40   35   20   25
Proportion of the arsenic added which
was precipitated, per cent. 75.2 63.9 12.0 7.8 7.8 4.3 2.5 0.2

These results show the possibility of contamination of the phospho-molybdate by arsenic if the temperature exceeds 25° C. While differing degrees of dilution, etc., seem to affect the percentage of arsenic precipitated, at 25° C., I have never found it to exceed the limits of error of a phosphorus determination.

The Ratio of Phosphorus to Molybdic Acid in the Ammonium Phospho-Molybdate.—A quantity of ammonium phospho-molybdate was carefully prepared at 25° C. by the addition of microcosmic salt to an ammonium molybdate solution. This was carefully washed by decantation with water, until the final decantation contained less than 0.00001 per cent. of the original solution, then transferred to a porcelain evaporating dish and dried at 85° C. to 90° C. for three days, with no contamination by organic matter. The result was a fine pulverulent yellow salt, with no tendency to caking, showing no sodium, and completely soluble in ammonium hydrate to a clear, colorless solution.

The phosphorus was determined:

1. By direct precipitation of the ammoniacal solution with magnesium mixture.

2. By Hundeshagen's method of freeing the solution from molybdic acid before precipitation of the ammonium magnesium phosphate, by the saturation of the ammoniacal solution with

H$_2$S, acidulation with HCl, and filtering from the precipitated MoS. After this treatment, less than 0.02 per cent. of molybdic acid remained in the solution. The resulting determinations of phosphorus were as follows:

By method 1, 1.622 and 1.625 per cent.; by 2, 1.626 and 1.631 per cent.; average of all, 1.626 per cent.

The molybdic acid was determined by precipitation as lead molybdate (PbO,MoO$_3$) and lead phosphate (Pb$_3$,PO$_4$) by lead acetate in an acetic acid solution, washing by decantation with boiling water, filtering on a weighed paper, and drying it at a 100° C. to 120° C. The final decantation showed no trace of lead, proving the mixed salts to be insoluble in boiling water. The resulting determinations of molybdic acid were 90.334 per cent. and 90.287 per cent.; average, 90.315 per cent.

The yellow salt, dried at 150° C., lost 0.99 per cent. of water. Further drying for fourteen hours, at 180° C., gave no additional loss, and, notwithstanding the ammoniacal solution was slightly blue in color, titration with a dilute solution of K$_2$Mn$_2$O$_8$ showed that no perceptible reduction of molybdic acid had taken place.

These results would give the phospho-molybdate the following composition :

		Per cent.
(NH$_4$)$_6$O$_3$	······································	4.091
P$_2$O$_5$	·······································	3.724
MoO$_3$	······································	90.315
H$_2$O	·······································	0.990

And the ratio of phosphorus to molybdic acid = 1.80 per cent.

In view of the difficulties attending the analysis of this salt and the well-known law of chemical reactions that the ratio between combining atoms is simple, it seems rational to assume that the composition of the salt corresponds to the formula (NH$_4$)$_6$O$_3$,24MoO$_3$,P$_2$O$_5$, with a percentage composition of :

	Per cent.	Per cent.
(NH$_4$)$_6$O$_3$	················ 4.101	
P$_2$O$_5$	················ 3.733	Phosphorus = 1.63
MoO$_3$	················ 90.849	

Ratio of phosphorus to molybdic acid = 1.794 per cent.

Reduction of Molybdic Acid.—In reducing MoO$_3$ preparatory to its oxidation with K$_2$Mn$_2$O$_8$ I use a modified form of Jones's

reductor, consisting of a tube about $\frac{5}{8}$ inch internal diameter, filled with powdered zinc to about six inches.

The reduction seems to be more perfect than with the addition of zinc to a sulfuric acid solution, as used in Emmerton's original method.[1] With a $K_2Mn_2O_8$ solution (one cc. $= 0.006703$ iron), I obtained the following determinations of $K_2Mn_2O_8$, corresponding to 0.5 gm. of phospho-molybdate, viz.: 77.14, 77.15, 77.10, 77.15, 77.20; average, 77.15 $K_2Mn_2O_8$. Assuming the salt to contain 1.63 per cent. of phosphorus, and the ratio of phosphorus to molybdic acid to be 1.794, molybdic acid $=$ iron $\times$ 87.847.

A number of determinations were made with varying quantities of molybdic acid, and all ranged from eighty-seven to eighty-eight. For the purpose of comparing these results with Emmerton's, the following determinations were made, as in Emmerton's original paper, using twenty gms. of zinc for reduction. The results from 0.5 gm. of phospho-molybdate were: $K_2Mn_2O_8$, 74.65, 74.65, 74.60; average, 74.63. This gives molybdic acid $=$ iron $\times$ 90.814 as against the theoretical value of 90.76. This would make the solution of $K_2Mn_2O_8$, one cc. $= 0.006436$ iron $= 0.0001$ P, instead of one cc. $= 0.006141$ iron $= 0.0001$ P.

If the MoO_3 were reduced to Mo_2O_3, we should have $MoO_3 =$ iron $\times$ 85.714. Hence the reduction seems to be at an intermediate point between Mo_2O_3 and $Mo_{12}O_{19}$, the formula quoted by Emmerton from Werncke for the sulfuric acid and zinc reduction.

This is an interesting point, and I should be glad if other members of the Institute felt disposed to make comparative tests.

Speed of Reduction.—Incidental to the reduction with $K_2Mn_2O_8$, I noted the effect of the speed of reduction and the rate of oxidation of the reduced solution when exposed to the air.

Varying the speed of reduction of a 200 cc. solution acidified with ten cc. sulfuric acid from twelve minutes to two minutes, I found the results to be coincident. With greater speed the reduction was less complete, so that in one case, where the time was thirty seconds, nearly ten per cent. escaped reduction.

The reduced solution, after standing exposed to the air for thirty minutes, showed no oxidation.

Temperature.—To determine whether all the phosphorus was

[1] Transactions A. I. M. E., 15, 95; this Journal, 1, 93.

precipitated at 25° C., whether the ratio of phosphorus to molybdic acid remained constant regardless of the temperature of precipitation, and whether the presence of $Fe_2(NO_3)_6$ had any effect on the composition of the phospho-molybdate, 0.100 phosphorus was added to a steel solution and precipitated at 25° C. and 85° C., the proper checks being made on the steel at those temperatures. The results were:

	Phosphorus. Per cent.
At 25°	0.101
At 85°	0.103

The difference is within the limits of experimental error, and shows that all the phosphorus is precipitated at 25° C. with five minutes' shaking, and that the composition of the phospho-molybdate is constant.

ON THE ESTIMATION OF ARSENIC AND PHOSPHORUS IN IRON ORES.[1]

BY JOHN PATTINSON, F. I. C., AND H. S. PATTINSON, PH.D., F.I.C.

Some iron and manganese ores contain very notable quantities of arsenic, and in estimating phosphorus in such ores, by either the ammonium molybdate or the magnesia process, it is necessary first of all to remove the arsenic; otherwise some of this substance is precipitated along with the phosphorus and makes the phosphorus determination too high.

The usual procedure in estimating phosphorus in ores, etc., containing arsenic is to dissolve the mineral in hydrochloric acid, evaporate the solution to dryness, to render the silica insoluble, then to take up the residue again with a minimum quantity of hydrochloric acid, filter from the silica, and reduce the ferric chlorid in the filtrate to the ferrous state, after which hydrogen sulfid gas is passed through the solution until it is saturated, in order to remove the arsenic. The solution is then allowed to stand for some hours or over night, and at the end of that time the precipitate of arsenic trisulfid is filtered off. The phosphorus is now determined in the filtrate, which is free from arsenic.

[1] *J. Soc. Chem. Ind.*, 12, 119.

There are many methods of estimating the phosphorus, but one of those most frequently used is to oxidize a small quantity of the ferrous iron in the solution, or to add a few drops of a solution of ferric chlorid to it and, after neutralizing the excess of acid present with ammonia, to precipitate the phosphorus as ferric phosphate by the addition of ammonium acetate. The precipitate, which contains the whole of the phosphorus, is then filtered, and the phosphorus determined in it either by the ammonium molybdate or the citric acid and magnesia method.

This process is tedious and consumes much time. By introducing three modifications into it we have succeeded in shortening very considerably the time required for making a determination of phosphorus in iron ores, etc., that contain arsenic. These three modifications are: (1) The reduction of the ferric chlorid solution with *sodium thiosulfate* (hyposulfite); (2) the precipitation of the arsenic with *zinc sulfid;* and (3), the precipitation of the phosphorus as ferric phosphate with *calcium carbonate.*

In carrying out our process we dissolve three gms. of the ore in hydrochloric acid, evaporate to dryness to render the silica insoluble, and take up the residue with as little excess of hydrochloric acid as possible. We then rinse the cover and sides of the beaker with hot water, taking care not to let the total volume of liquid exceed thirty to fifty cc. We now reduce the ferric chlorid by adding gradually to the cold solution a solution of sodium thiosulfate, made by dissolving about 500 gms. of this salt in a liter of distilled water. This solution may be added somewhat rapidly at first, but towards the end of the reduction it should be added slowly, drop by drop, until one drop fails to produce any violet color of ferric thiosulfate. If the thiosulfate has been added very rapidly, a brownish yellow color often remains in the liquid, even after the iron has all been reduced to the ferrous state, but this color is of no importance and gradually disappears if the solution is allowed to stand for a few minutes. If the thiosulfate be added somewhat more slowly at the end of the reduction the solution is usually colorless, or has merely the greenish color of a solution of ferrous chlorid.

If a large excess of hydrochloric acid has been present, a considerable evolution of sulfurous acid occurs during the addition

of the thiosulfate, but if, as should be the case, there is only a small excess of acid, very little sulfurous acid is evolved.

After the iron has been reduced, if the volume of the liquid be less than fifty to sixty cc., it must be diluted to this volume, and it is then boiled to expel the whole or the greater part of the sulfurous acid retained in the liquid. If care has been taken not to add too much thiosulfate in excess, and only a moderate quantity of hydrochloric acid is present, the sulfurous acid is expelled after only a few minutes boiling. If the solution be allowed to boil too long, so that it becomes much more concentrated, or if it be not diluted to about fifty to sixty cc. before boiling, sulfur will often separate. This does not affect the accuracy of the process, but it sometimes makes the subsequent filtrations rather slower. But usually no sulfur separates, and the sulfurous acid having been expelled, the solution is then cooled and five cc. of concentrated hydrochloric acid added to it. We prefer to have the bulk of liquid, after addition of the five cc. of acid, about sixty to eighty cc., and it should not at the most be more than 100 cc. A little powdered zinc sulfid (about 0.1 gm.) is now shaken from the point of a spatula into the cold, strongly-acid liquid. If arsenic be present an immediate precipitate of arsenic trisulfid forms and collects together on gently agitating the liquid. The hydrogen sulfid in the beaker should be blown out, and if after agitating the liquid a strong smell of the gas is not noticed, a little more zinc sulfid should be added. If all the sulfurous acid has been boiled off, no sulfur precipitates on adding the zinc sulfid, and in this case very minute quantities of arsenic trisulfid can be detected, as little as 0.001 gm. being distinctly observable. If sulfurous acid be present the sulfur that separates masks the precipitate of small quantities of arsenic trisulfid. The expulsion of the sulfur dioxid is not essential, but if much be present, the expulsion of at least the greater part is to be recommended, as often any time saved by not boiling it off is afterwards lost by the slower filtration due to separated sulfur. But if the arsenic has to be determined, the boiling of this concentrated ferrous chlorid solution ought not to be prolonged beyond three or four minutes, as on long continued boiling there is a loss of arsenic due to volatilization of As_2Cl_4. With a little practice the reduction can readily be effected so that

practically the whole of the sulfur dioxid is expelled by boiling for less than this time.   It must also be noted that when the arsenic has to be determined in ores containing ferrous oxid, such ores must be oxidized before evaporating to dryness, otherwise arsenic is lost during the evaporation. If copper be present, this, too, is precipitated by the zinc sulfid and makes the precipitate of arsenic trisulfid appear brown, but lead is not precipitated owing to the excess of acid in the solution.   Puller (*Ztschr. anal. Chem.*, 1871, 41) showed that arsenic trisulfid was only completely and speedily precipitated from a solution of arsenious acid by hydrogen sulfid when the solution was very strongly acid.   Working with an excess of only one cc. of acid in seventy cc. of liquid, we have in some cases found that the arsenic was completely separated at once by zinc sulfid, but in other cases with only this small excess of acid we have found that all the arsenic did not come down immediately, whereas with five cc. of acid in excess we find that the quantity of arsenic ordinarily met with in iron ores, etc., is always removed at once.   If the quantity of arsenic present be very large, requiring an unusual addition of zinc sulfid, it is better to add ten cc. of acid in excess instead of five cc., since it must be borne in mind that the zinc sulfid gradually neutralizes the acidity of the solution.   If the volume of liquid be more than 100 cc. we also find that the complete separation of the arsenic is uncertain, unless the solution be allowed to stand some hours.   It is advisable to cool the solution before adding the zinc sulfid, otherwise the evolution of hydrogen sulfid is too violent, and an unnecessary quantity of zinc sulfid has to be used to effect saturation.

The precipitate of arsenic trisulfid, together with the silica in the sample, is now filtered, for which a loose-textured filter paper should be used.   It filters rapidly if the quantity of silica be not very large, and if much sulfur has not been precipitated, which latter contingency will not exist if the precautions we have indicated have been followed.   The precipitate, when lead is present in the ore, should be rinsed upon the filter and washed two or three times with warm water acidulated with five cc. of hydrochloric acid in 100 cc.   This keeps the lead sulfid in solution. The precipitate may then be given three or more washings with

hot water, which is enough to remove all but a trace of the iron. The filtrate is now boiled to expel the hydrogen sulfid; it is then diluted with cold water to about 200 to 250 cc., and a sufficient quantity of ferric chlorid solution added to combine with all the phosphorus and leave a slight excess of ferric iron. If now the usual method of precipitating the ferric phosphate be adopted, *viz.*, by neutralizing the excess of acid with ammonia and then adding ammonium acetate and boiling, it will be found that the addition of ammonia to the solution causes at once a considerable precipitate of sulfur, a fact which points to the formation of pentathionic acid in the process. In order to avoid this precipitation of sulfur we were led to use precipitated calcium carbonate to throw down the ferric phosphate. This not only avoids the separation of sulfur, but precipitates the ferric phosphate in a bulky, flocculent form, which filters much more rapidly than the precipitate produced by ammonium acetate, which is very often slimy and clogs the pores of the filter paper, so that much time is wasted in filtering it.

When using calcium carbonate we find the precipitate of ferric phosphate comes down in the best form for filtering when the temperature of the solution is about 65° to 70° C. We throw the calcium carbonate into the liquid from the end of the spatula, taking care to rapidly replace the glass cover on the beaker to avoid loss by effervescence, and after each addition of calcium carbonate we give a circular motion to the liquid in the beaker until the whole of the ferric phosphate and the excess of ferric hydrate are precipitated. Care should be taken to avoid the addition of more than a very small excess of calcium carbonate. With an excess of five cc. of hydrochloric acid about three gms. of the carbonate are required to neutralize the acid and precipitate the ferric phosphate. The calcium carbonate should be free from phosphorus. The precipitate of ferric phosphate formed in this way filters rapidly, and it has also the advantage of dissolving rapidly in dilute nitric acid, which is the next operation if it be desired to precipitate the phosphorus as ammonium phospho-molybdate. It should, however, be washed with warm water and not with boiling water, as in the latter case it is rendered less easily soluble. When dissolving the precipitate of

ferric phosphate in acid, off the filter paper, a glass cover should
be held over the funnel to avoid any loss caused by the efferves-
cence from the small excess of calcium carbonate mixed with the
precipitate.

Instead of precipitating the arsenic with zinc sulfid, hydro-
gen sulfid gas may of course be used, and if the bulk of the
liquid be less than 100 cc. and the proper quantity of acid be
present, the whole of the arsenic can be entirely separated in a
quarter of an hour. Zinc sulfid is, however, much handier. It
may be bought as a powder, or it may be made in the labora-
tory by precipitating with hydrogen sulfid from a hot acetic acid
solution, washing the precipitate by decantation, drying at 100°
C., and finally pounding it in a mortar. It should be free from
other metals precipitated by hydrogen sulfid in acid solution, and
from phosphorus.

If it be desired to determine the amount of arsenic, the precipi-
tate of arsenic trisulfid, after being washed, should be dissolved
in ammonium sulfid. When much silica is present in the ore, it
is difficult to remove all the arsenic by pouring the ammonium
sulfid on the filter, and we find it best to rinse the precipitate off
the paper into a beaker with a jet from a wash bottle containing
ammonia, and then to digest in the beaker with ammonium sulfid,
allow the silica to settle, filter off the clear liquid, and digest
again, and finally to transfer the siliceous residue to the filter
paper once more and wash with ammonia. The ammoniacal
solution is then evaporated to dryness on a water bottle and the
residue oxidized with a few drops of concentrated nitric acid and
a drop of bromin. This is again evaporated to dryness or to an
oily consistency, taken up with a little hydrochloric acid, ammo-
nia added, and any silica present filtered off. The arsenic is then
precipitated in the filtrate by magnesia mixture, collected on a
weighed filter paper, and dried at 100° C. An addition of 0.001
gm. should be made to the weight of the precipitate for every
sixteen cc. of liquid in which the arsenic was precipitated, to com-
pensate for the solubility of the ammonio-magnesium arsenate.

The following are some of the results we have obtained, which
show the satisfactory working of our method. The phosphorus
in every case was weighed as ammonium phospho-molybdate.

Arsenic taken, gm.	Phosphorus taken, gm.	Arsenic found, gm.	Phosphorus found, gm.
0.010	0.00216	0.0094	0.00215
0.010	0.00216	0.0095	0.00216
0.010	0.00216	0.0100	0.00218
0.0060	0.0028	0.0059	0.0027

In each of the above experiments a solution of ferric chlorid containing about 1.5 gm. of iron was taken, to which the known quantities of arsenic and phosphorus were added in the form of solutions of arsenious acid and sodium phosphate. The arsenious acid was then oxidized with bromin water, and after boiling off the excess of bromin the arsenic and phosphorus were determined as described.

We have made numerous analyses of iron ores, manganiferous iron ores, and manganese ores, steel, and cast iron by this method, and it is in daily use in our laboratory.

We find that after the sample has been dissolved and evaporated to dryness we are able by this method to complete an estimation of phosphorus in ores, etc., containing arsenic, in from an hour and a half to an hour and three-quarters.

PATENTS OF INTEREST TO CHEMISTS.

Arno Behr treats Indian corn in aqueous solution with sulfurous acid, separates the starch as usual, adds sulfuric acid to the steeping water, evaporates, and adds an absorbent to form a rich cattle food (491,234).

Bernhard Lepsius heats a mixture of picric acid with some enveloping explosive agent, such as tri-nitrotoluene, in a mould, at a temperature above the fusing point of the latter and below that of the former, thus cementing together the picric acid for use in projectiles (492,089). To coat metals (491,220) Wm. Mild dips the metal first in warm dilute sulfuric acid, next rinses in cold water, then immerses in a bath containing 200 pounds hydrochloric acid, two pounds ammonium chlorid, ten pounds zinc spelter, and drys. The bath used for finally coating the metal contains the following proportions per ton: 1300 pounds

lead, 700 pounds block tin, half pound bismuth, six ounces sodium, and two pounds of ammonium chlorid, and the solution in which the article to be coated is finally dipped contains one pound of ammonium chlorid in forty gallons of boiling water. Viggo Drewsen (492,196) has an apparatus for regenerating sulfurous acid from the waste gases in manufacturing sulfite pulp.

David A. Wray (491,395) uses tar or the residuum, or heavier products of oils, mixed with chlorid of sulfur and chlorid of iron, for a roofing and paving composition. Ludwig Haarmann secures a surface of asphaltic mastic by first coating with a solution of a bituminous substance, and applying mastic after evaporation of the solvent (492,197). A new compound of blown oils is described as "blown, non-drying glycyl ether of an unsaturated fatty acid, combined with pyroxylin or nitro-cellulose," and Walter D. Field is the patentee (491,880). Plumbago, white lead, litharge, and asbestos, and a binding or cementing substance as resin, or gum copal in linseed oil, is claimed by John T. Richards as a composition for journal bearings (492,750).

A milk coagulating product is patented by Clarence P. Eyre, but the description is exceedingly vague as to the nature of the ferment used (491,416).

Benedickt Ehman employs a mixture of gasolene, sulfuric ether, alcohol, spirits of ammonia, powdered borax, powdered carbonate of soda, and saltpeter, for removing grease (491,413). Gustav Gumbel uses the waste liquors from the manufacture of sulfite cellulose, glue, and hydraulic lime, as a compound for "water-proofing oil receptacles" (491,284). Aluminum dissolved in glacial phosphoric acid, mixed with zinc oxid, which has been first heated to reduce to a gummy condition, forms a base for a dental cement, which Max Sichel covers by 492,056. A cement composed of pulverized spent lime, pulverized carbon, silica, iron oxid, alumina, lime, magnesia, slaked rock lime, and sand is the invention of Bernard Dreyfuss (491,280).

James L. Covel describes his material for covering pipes as consisting of wheat flour, pulverized alum, arsenic, red lead, litharge, beef gall, and water (491,836). Richard V. Mattison has taken out three patents, one (492,092) is for a non-heating composition composed of calcium carbonate, magnesium carbonate,

and asbestos, the second (492,093) is a boiler covering composition, containing magnesium carbonate, plaster of Paris, asbestos, and wood pulp, and the third is similar (492,094) with the exception that calcium carbonate is substituted for the plaster of Paris.

Alfred E. Hunt manufactures steel in the following way (493,090): The iron is first refined, and to it a deoxidizing agent is added; then the refined metal is recarburized by the addition of free carbon in sticks in definite proportions. Norman K. Morris and John W. Bailey manufacture white lead by two processes. The first (493,173) consists in pulverizing lead carbonate and hydrated lead oxid and mixing with a volatile oil of the petroleum type; 493,106, the second, is described as first forming lead fiber into independent masses, charging with acetic acid by dipping and then exposing to the action of carbon dioxid and aqueous vapor. Bernhard Rösing (494,349) brings a molten oxygen compound of lead, as litharge, in contact with a sulfid as galena in order to separate the metal. Carl V. Petraeus (492,832) smelts lead ores in a low cupola furnace; pulverized galena in admixture with air is injected into the upper part of the furnace, and the resultant fumes are screened, making a lead pigment.

Robert R. Graf uses tungstate of ammonium, hyposulfite of ammonium, sulfate of soda, caustic lime, chalk, alum, carbonate of soda, and oil for a fire-proof paint, (494,508). John K. Hawkins (493,999) dissolves resin in benzine or gasoline, places this solution in contact with lime treated with water, pours off the solution from the lime and mixes with a solution of dissolved rubber or gutta percha. Eugen Schaal patents a process and apparatus for thickening linseed oil (493,187). The oil is heated to 320°–345° C., a current of indifferent fluid is kept on the surface of the heated oil, while fresh oil is fed into the lower portion of the heated mass and the thickened oil flows off from the top. 492,836 is a method for the treatment of sole leather (Frederick Riegert, patentee). The leather is first treated in a hot bath of beeswax and spirits of turpentine or benzine, then removed from the bath and subjected to a pounding action. Julius Dubiel has a process for the manufacture of starch (493,689).

Moses Wool is granted 493,460 for a process for making brandy-mash and composition for same. and electricity is used by John Becker for purifying and ageing liquors (493,809).

An antiseptic and antineuralgic compound, derived from salicylic acid, is patented by Herman Janssen (492,868). It has the formula

$$C_6H_4 \underset{\displaystyle COO - C_6H_4 - N}{\overset{\displaystyle OH}{\diagup}} \underset{\displaystyle COCH_3}{\overset{\displaystyle H}{\diagup}}$$
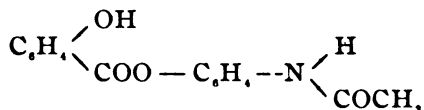
Peter T. Austen adds a solution of a nitrite to logwood chips to cure them (494,237).

There are a number of new dyes patented. Bruno R. Seifert obtains a dye from alpha oxyuvitic acid (493,143); Herman Boedeker, a pink dye, the alkali salt of a sulfonic acid, derived from fluorescein chlorid and mesidine (493,241). Jakob Schmid has a blackish blue azo-dye, 493,563, and a gray-black tetrazo-dye, 493,564, and Jakob Schmid and Robert Gnehm patent a red azo-dye (493,583). Mr. Schmid and R. Paganini prepare mono-sulpho-dioxynaphthoic acid by heating the sodium salt of di-sulpho-beta-oxy-naphthoic acid with caustic alkalis at 200° to 260°, and precipitating the dissolved melt with hydrochloric or sulfuric acids (493,562). Charles Noroy (493,286) first dips goods to be dyed black into a bath of water, logwood, and a copper salt, then immerses in a fixing bath, composed of "neutralized nitrated starch," alum, metallic sulfates, potassium bichromate, and a small quantity of soda or ammonia.

Air-slaked lime, glue, or oil cake, and china clay, are the ingredients of a compound used by Enos A. Bronson for retarding the setting of plaster (493,613), and Caroline S. Ely (493,693) names soda ash, ammonium sulfate, borax, oat and wheat flour, as a washing compound. R. B., J. L., and R. W. McEwen patent a process for forming paper board from old newspapers (492,927). Frank S. Culver patents a fire-proofing composition for wall covering containing asbestos fiber, clay, plaster of Paris, "Acme" cement and a binding fiber (493,152) and James F. Thompson has a new burnishing composition (494,514). John F. Newell receives two patents on compositions for bearings. 494,156

mentions plumbago, fibrous substance, red lead, white lead, and a drying oil; and 494,433, plumbago, fibrous substance, an oxid, carbonate or basic carbonate of lead.

[The specification and drawing of any U. S. Patent in print may be obtained from the publisher of this Journal. Applications must be accompanied in all cases by twenty-five cents for each patent specification wanted. BE CAREFUL TO WRITE THE NUMBER LEGIBLY.]

NOTES.

Letter from Mr. Melvil Dewey.—The following letter has been sent to each member of the Committee on Spelling and Pronunciation of Chemical Terms, by Mr. Melvil Dewey, Secretary of the New York State Board of Regents.

Regents' Office, Albany, N. Y., March 24, 1893.

TO THE COMMITTEE ON SPELLING AND PRONUNCIATION OF CHEMICAL TERMS:

I wish to express the gratitude of all thoughtful people for the splendid piece of work your committee has done in simplifying chemical terms. I am greatly surprised, however, by the statement I see to-day that you recommend the spelling "gramme" because of the danger of confusing it with "grain" in ordinary writing. For twenty years I have been known as the apostle of the metric system, and have given much attention to the subject, and I was startled that your committtee should have accepted such a reason and recommended a spelling which the metric advocates have vigorously denounced for all these years and which we have so largely driven out of common use. Possibly I am misinformed, and I send this letter to each of the committee asking any needed correction and for the opinion of each on the solution here offered. We always told physicians to write g. for gramme and gr. for grain, and uniformly to write metric prescriptions with the decimal line. The g. and gr. might be stupidly mixed, but no one could confuse the decimal line with the characters of the ordinary prescription. This is shorter than to write cg. and mg. for the smaller weights and is the safest and most compact possible form. Would not your committee be willing to recommend this and withdraw the gramme form? I ask this because I am about to print your report in full for distribution through the 500 institutions of the state, and I hesitate to include a recommendation so contrary to my best judgment and to the results of our study of this question.

Yours very truly,

MELVIL DEWEY.

Another Convert.—"Hereafter the *Popular Science News* will adopt the system of chemical nomenclature recommended by the committee of the American Association for the Advancement of Science. None of the changes are very radical, but they are in the direction of a rational system, and, as far as they go, an improvement upon the existing one. The most notable change is in the spelling of the element sulphur and its derivatives. The letters *ph* are changed to *f*, and the new forms, sulfur, sulfate, etc., seem to be a commendable change, although it is a pity that the reform was not also applied to phosphorus and its compounds. The final *e* is dropped from chlorine, bromine, iodine, and aniline; cæsium is changed to cesium, and the final *e* is also dropped from all terminations in *ide*, such as oxide, chloride, etc. Glycerin will hereafter be known as glycerol, while, to make matters even, benzol is changed to benzene. The termination *ic* is used for metals only where necessary to contrast with *ous*. Thus, ferric and ferrous salts are known, but as there is only one series of salts of ammonium, instead of the old form ammonic chloride we have ammonium chlorid. The above are the most noticeable changes, although there are many minor ones; and if our readers will pardon occasional 'reversions' at first, we hope to have the new nomenclature successfully adopted in the course of two or three numbers."—*Popular Science News*, March 1, 1893.

Determination of Crude Carbolic Acid. By G. Schacherl.—The usual commercial method of determining the value of crude carbolic acid is to determine the solubility in caustic soda of sp. gr. 1.2. That this process does not give reliable results has already been frequently proved.

A better plan is to adopt the following method : 100 cc. of the poorer kinds of carbolic acid, which are only slightly soluble in caustic, or fifty cc. of the better kinds, which dissolve to the extent of at least one-half, are employed. The measured carbolic acid is twice shaken in a separating funnel with 100 cc. of caustic soda of sp. gr. 1.1, and then three times In addition with quantities of fifty cc. (The alkaline liquid obtained in the last shaking should give no oily drops on the addition of hydrochloric acid.) The different extracts are united in a flask of about one liter

capacity, and contain all the phenol, small quantities of hydro-carbons, and more or less resins. The liquid is diluted with an equal volume of water and distilled until no more oily drops pass over, and the distillate appears perfectly clear ; the hydrocarbons are in this way removed. The contents of the flask are then allowed to cool, acidified with commercial hydrochloric acid, and again distilled, a large Liebig condenser being employed. The phenols pass over and condense along with the water in the re-ceiver. When about 200 cc. have come over the distillation is interrupted, the water which has passed over poured back into the flask, and the phenol brought into a graduated cylinder. The dis-tillation is then repeated, any oil which passes over being added to that in the cylinder, and this is done until no more oil passes over with the distillate. The final distillate, which amounts to about sixty to seventy cc., is saturated with common salt, and the phenol which separates out measured, and its amount added to that already obtained in the cylinder.

The following numbers show the difference between the results obtained by the commercial method and those given by this modi-fied plan, the numbers in parentheses being those obtained by Schacherl : 35 (25) per cent., 52 (48) per cent., 53 (47) per cent., 70 (66) per cent., 100 (74) per cent., 100 (82) per cent., 100 (97) per cent., and 100 (98) per cent. The commercial method, there-fore, always gives a larger amount than is really present.—*Ztschr. Osterr. Apoth., through Chem, Trade Journal.*

Benzene from Semet-Solvay Coke Ovens.—The Compagnie des Mines de Crocourt in the north of France, has just started working five of these ovens and 150 others on the same system will within a few weeks be put in operation by the following companies :— Société des Charbonnages des Kessales, near Liège ; Société John Cockerill, at Seraing, and the Phoenix Company, at Laar, near Ruhrort. These two hundred ovens will have a *minimum* production of 24,000 gallons of 90's benzol per month, though it is more likely the monthly turnout will reach nearer 36,000 gallons. Adopting the former figure, however, we shall have nearly 300,000 gallons of benzol on the market in a year, in addition to the usual supply. The introduction of this additional quantity is not likely to improve the price of this commodity.—*Chem. Trade Journal.*

=====THE=====

JournalofAnalytical&AppliedChemistry.

ACID CALCIUN SULFATE.

BY H. ENDEMANN, PH.D.

IF we dissolve potassium bisulfate in water, we have not
merely a solution of this salt in water, but a solution of neu-
tral potassium sulfate, acid potassium sulfate, and free
sulfuric acid.

   If the solution thus prepared is sufficiently concentrated
and has been heated we obtain on cooling crystals of neutral
potassium sulfate.   That this body has not been formed
solely by reason of its insolubility may be shown by preparing
a solution with the addition of some sulfuric acid, which prevents
the separation of the neutral salt.

   If then the water produces the decomposition of the salt it is
evident that dilution with water must still increase it.   In fact, it
has been determined that such is the case and this has been
demonstrated by the fact that on diluting a solution of acid
potassium sulfate heat is produced.   A solution of forty gms. in
one liter of water liberates 330 calories per equivalent.   From
this it can seen that the rise of temperature, while it can be
measured, is not great and requires careful work in order that it
may be estimated.

   To come now to the acid calcium sulfate we find it stated in
the text books, that it is prepared by dissolving calcium sulfate
in hot sulfuric acid and allowing the mixture to cool, when the
acid sulfate will crystallize out.   Water, it is stated, decomposes
it into neutral sulfate or gypsum and free sulfuric acid.   The

question which I set out to determine was this: Is the reaction of acid calcium sulfate really so simple, or does the acid sulfate follow, within limits, (due to the much greater insolubility of the neutral sulfate) in its decomposition with water, the reaction as outlined for the acid sulfates of the alkalis.

A preliminary experiment showed in the first place that the hydrated calcium sulfate is more soluble in water containing free sulfuric acid, than in pure water.

1000 parts of water dissolve at			0° C.		2.05 parts.
1000 " " "		"	"	35° C.	2.54 "
1000 " " "		"	"	100° C.	less than 2 parts.

In water containing between one and two per cent. of sulfuric acid, the solubility was found to be at 13° C., 2.45 parts; at 80° C. 7.11 parts.   As in the case of the alkalis, we can therefore prevent the separation of the neutral sulfate by the addition of acid.

From this experiment, however, considering the still very limited solubility, it becomes at once evident that if the determination of the dissociation of the acid potassium sulfate is a very delicate operation, it must in the case of the acid calcium sulfate be still more difficult and almost hopeless, provided that no other than the thermo-chemical method mentioned is at hand.   I found a ready means, however, by a chemical method, which forms the subject of this paper.

It is a well known fact that solutions of dextrin when heated with dilute sulfuric acid yield glucose.   The amount of glucose is dependent upon the concentration of the acid, the temperature, and the time of treatment.   I argued that if salts are added to a sulfuric acid solution which will chemically bind some of the sulfuric acid, the quantity of sugar formed will be less.

With this object in view the following experiments were made.

I examined the action of sulfuric acid upon artificial gum (soluble starch) by itself, and in admixture with potassium sulfate and calcium sulfate, and the degree of action of the mixtures upon the gum was measured by the quantity of copper thrown down as suboxid of copper from an alkaline copper solution.   A ten per cent. solution of gum was made and in this solution the quantity of sugar present was found to correspond to 12.5 mgms.

of copper for ten cc. of this solution. The following three mixtures were then prepared:

1. 20.2 cc. normal sulfuric acid solution, 80 cc. water.
2. 20.2 cc. normal sulfuric acid solution, 80 cc. water, 1.775 gm. potassium sulfate.
3. 20.2 cc. normal sulfuric acid solution, 80 cc. water, one gm. crystallized calcium sulfate.

All three mixtures were brought on a hot water bath, common to all, where they remained for one hour to give the third solution time to saturate itself with gypsum, of which there was a decided excess present which was left in the solution during the subsequent treatment.

Each of these solutions then received ten cc. of the artificial gum solution (= one gm. of gum), and remained an equal time (about one hour and a quarter) in the water bath, and the sugar formed was then determined. The following was the result of the treatment in one-eighth of the total (twenty-five cc. from 200 cc., to which the solution had been diluted).

No. 1 gave total copper 0.0383
Due to sugar in gum 0.0125
_____
Due to sugar formed 0.0258
No. 2 gave total copper 0.0231
Due to sugar in gum 0.0125
_____
Due to sugar formed 0.0106
No. 3 gave total copper 0.0314
Due to sugar in gum 0.0125
_____
Due to sugar formed 0.0189

Sulfuric acid alone had therefore produced sugar sufficient to reduce 206.4 mgms. copper; in presence of potassium sulfate 84.8 mgms. copper; in presence of calcium sulfate 151.2 mgms. copper; or the two latter respectively 41.1 per cent. and 73.3 per cent. of what the sulfuric acid alone had been capable of producing. There had been no attempt made to make these reactions anyway with reference to atomic proportions; with this in view the experiments were repeated, using different proportions:

1. 20 cc. normal sulfuric acid, 80 cc. water.
2. 20 cc. normal sulfuric acid, 80 cc. water, 0.566 potassium sulfate.
3. 20 cc. normal sulfuric acid, 80 cc. water, 0.56 crystallized calcium sulfate.

To each of these were added ten cc. of the ten per cent. gum solution after the solution had been heated for one hour to obtain a complete solution of the calcium sulfate, in which, however, I did not quite succeed. The heating was then continued on a steam bath for two hours, and the solutions neutralized, respectively the lime removed by carbonate of soda, and the solutions brought to 200 cc. The reducing power of the solutions was tested with twenty-five cc. each.

<div style="text-align:center">

No. 1 gave total copper ····················· 0.0400
Due to sugar in gum ··················· 0.0125

Due to sugar formed ··················· 0.0275

No. 2 gave total copper ····················· 0.0335
Due to sugar in gum ··················· 0.0125

Due to sugar formed ··················· 0.0210

No. 3 gave total copper ····················· 0.0350
Due to sugar in gum ··················· 0.0125

Due to sugar formed ··················· 0.0225

</div>

Sulfuric acid alone had therefore produced sugar sufficient to reduce 0.220 copper; with potassium sulfate, 0.168 copper; with calcium sulfate, 0.180 copper.

Considering the fact that I had not been able to get all the calcium sulfate into solution even towards the end of the experiment, I believe that the results warrant the statement that the acid calcium sulfate can exist in dilute solutions, and that, as far as its limited solubility does not interfere, it follows the same laws as other bisulfates.

I wish yet to add that this investigation was undertaken for the purpose of moderating the action of sulfuric acid for technical purposes, where it was not desirable to moderate the action by still greater dilution, and that the practical results have in fact proved that the views which led to this investigation were correct not only for temperatures below 100° C., but by experiments under pressure at temperatures corresponding to such pressures.

THE ELECTROLYTIC SEPARATION OF MERCURY FROM BISMUTH.

BY EDGAR F. SMITH AND J. BIRD MOYER.

The question as to whether mercury can be completely precipitated by the current in the presence of nitric acid has been frequently discussed and answered in the affirmative. We observe, too, that in electrolytic literature it is this solution of mercury which has been generally recommended for the separation of the latter metal from various other metals associated with it. Thus, in the latest edition (the third) of Classen's *Quantitative Analyse durch Elektrolyse*, p. 147, the author, in describing the analysis of an alloy containing tin, lead, bismuth, and mercury, writes as follows:

"Aus der saltpetersauren Lösung (the filtrate from the tin oxide) kann man nun zunächst das *Quecksilber* und einen Theil des Bleies als Superoxyd auf der positiven Elektrode fällen. Um die vollständige Abscheidung des Bleies zu bewirken unterwirft man die von Quecksilber befreite Lösung nochmals der Elektrolyse, indem man die Schale mit dem positiven Pol des Stromerzeugers verbindet, verdampft zur Bestimmung des *Wismuths* die bleifrei Lösung zur Trockne und verfährt nach S. 81," etc., etc.

These instructions would most certainly lead one to infer that mercury can be separated in the electrolytic way from bismuth in the presence of nitric acid. Trials, qualitative it is true, were made by one of us (S) years ago; these indicated a co-precipitation of the metals from a nitric acid solution, and therefore we find in Smith's *Electrochemical Analysis*,[1] p. 97, the statement that "mercury cannot be separated in the electrolytic way from silver and bismuth." The recent experience of Smith and Saltar[2] with copper and bismuth confirms this last observation. That others may be convinced that these two metals—mercury and bismuth—cannot be separated electrolytically, when present in a nitric acid solution, we submit the results obtained lately.

We first experimented upon the solution of a mercury salt. It contained 0.1132 gram of metallic mercury in ten cc. of liquid.

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[1] P. Blakiston, Son & Co., Philadelphia, Pa.
[2] This Journal, 7, 128.

Experiment 1.

To ten cc. mercury solution (=0.1132 gram of metallic mercury) were added five cc. of nitric acid (sp. gr. 1.2), and then diluted with water to 180 cc. A current of 0.6 cc. electrolytic gas per minute was permitted to act upon this solution. The deposit of mercury weighed 0.1132 gram.

Experiment 2.

The quantity of metallic mercury was the same as in experiment 1. The volume of nitric acid (sp. gr. 1.2) was three cc.; the total dilution equaled 180 cc., and the current liberated 0.3 cc. electrolytic gas per minute. The precipitated mercury weighed 0.1137 gram.

Experiment 3.

The conditions were the same as in the preceding experiment, except that the volume of acid added equaled ten cc. and the current gave 0.3 cc. electrolytic gas per minute. The deposit of mercury weighed 0.1131 gram.

Experiment 4.

In this instance the only departure from the conditions observed in the preceding experiment was that fifteen cc. of acid were added to the solution undergoing electrolysis. The deposited mercury weighed 0.1131 gm. In appearance it was more drop-like than any of the previous deposits.

Experiment 5.

The conditions of experiments 3 and 4 were retained, but the volume of acid was increased to twenty-five cc. The precipitated mercury weighed 0.1083 gm. The filtrate showed the presence of unprecipitated metal. A second trial proved just as unsuccessful, but upon raising the current to one cc. electrolytic gas per minute, in two later experiments, with conditions otherwise the same as indicated above, the quantities of metal precipitated were

a .... 0.1130 gram.
b .... 0.1130   "

The precipitation was complete. We see, however, from the above that as the quantity of free acid is increased it is well to increase the strength of the acting current.

It will be understood that the current strength mentioned by

us in this article was that with voltameter and the electrolyte in circuit.

The deposits of mercury were washed with warm water and alcohol. They were dried by holding the dish in the hand and blowing gently over the metal surface, and also by standing over sulphuric acid for a brief period.

The bismuth solution employed by us was of such strength that ten cc. of it contained 0.1432 gram of metallic bismuth. The conditions of complete precipitation of this metal from nitric acid solution have already been given by Smith and Saltar.[1] We can therefore advance to an account of our experience in attempting to separate these metals.

Experiment 1.

Ten cc. of mercury solution (=0.1132 gram of metallic mercury), five cc. of bismuth solution (=0.0716 gram of metallic bismuth), and ten cc. of nitric acid of sp. gr. 1.2, were diluted to 200 cc. and electrolysed with a current that gave 0.4 cc. of electrolytic gas per minute. The weight of precipitated metal was 0.1821 gram. The anode was also covered with bismuth peroxide. The precipitation of metals was complete, but the mercury contained bismuth.

Experiment 2.

Preserving the conditions of experiment 1, but increasing the volume of acid to fifteen cc., the weight of the metallic deposit was 0.1850 gram. The anode also showed bismuth. Thus, again, *this metal appeared at both poles.*

Experiment 3.

Here the volume of acid was increased to twenty-five cc. and the current lowered to 0.2 cc. electrolytic gas per minute. The precipitation of. metals was incomplete, although bismuth was found at both poles. On repeating the experiment the precipitation was found to be incomplete.

Experiment 4.

The current was increased to 0.8 cc. electrolytic gas per minute. The precipitation was complete, but bismuth appeared at both poles.

[1] This Journal, 7. 12⁶.

Experiment 5.

In this experiment we observed the following conditions:

Ten cc. of mercury solution (=0.1132 gram of metallic mercury), two cc. of bismuth solution (=0.0358 gram of metallic bismuth), twenty-five cc. of nitric acid (sp. gr. 1.3), and total dilution of 180 cc., were electrolysed with a current liberating 1.5 cc. of electrolytic gas per minute. The precipitated mercury weighed 0.1441 gram. The positive pole was covered with bismuth peroxide. The mercury contained metallic bismuth. The precipitation of metals was complete.

Experiment 6.

With conditions the same as those of experiment 5 the precipitated mercury weighed 0.1445 gram; the anode was covered with bismuth peroxide.

Experiment 7.

In this trial the only change that we made from the conditions of experiment 6 was to reduce the quantity of bismuth to 0.0179 gram. The precipitated mercury weighed 0.1290 gram. It showed bismuth. The anode was coated with bismuth peroxide. The precipitation of metals was complete.

Experiment 8.

With conditions similar to those of 7, except that the current registered 1.4 cc. of electrolytic gas per minute, the precipitated mercury weighed 0.1284 gram. The anode showed bismuth peroxide. We found that the metals were precipitated simultaneously. Indeed, at times, it seemed that the precipitation of the bismuth began before that of the mercury. This was true with the most varying conditions. Hence, we believe that the conditions proposed by Classen (see quotation above) should be modified to accord with facts, as stated by us, and with his own personal observation, as recorded in the *Ber. d. chem. Ges.* (1886), **19,** 325:

"Von *Wismuth* konnte das Quecksilber auf diese Weise nicht getrennt werden. Beide Metalle scheiden sich gleichzeitig aus der sauren Lösung aus."

CHEMICAL LABORATORY OF
THE UNIVERSITY OF PENNSYLVANIA.
1893.

THE ELECTROLYTIC SEPARATION OF COPPER FROM ANTIMONY.

BY EDGAR F. SMITH AND D. L. WALLACE.

The separation of these two metals, in the electrolytic way, has long presented difficulties. These were first noticed by Wrightson (*Ztschr. anal. Chem.*, **15**, 297). Operating upon solutions containing 1.2075 per cent. of metallic copper and 0.280 per cent. to 0.800 per cent. of antimony, in the presence of twenty cc. of nitric acid of sp. gr. 1.21, and total dilution of 200 cc., he found that more or less antimony was precipitated together with the copper. Wrightson remarks, however, that in the presence of much less antimony (*e. g.*, in impure copper) it is possible to throw down the copper free from antimony. Classen corroborates this statement, and finds that the separation of copper and antimony may be made in a solution of the double oxalates (*Quantitative Analyse durch Elektrolyse*, dritte Auflage, p. 125), provided that the antimony content is very slight, and that the current is not permitted to act any longer than absolutely necessary for the complete deposition of the copper.

From the preceding statements it is manifest that a better, more certain, separation is desirable. In conjunction with Muhr (J. ANAL. APPL. CHEM., **5**, 488) one of us (S) found that iron, cadmium, copper, nickel, and other metals could be completely precipitated from ammoniacal tartrate solutions. The iron carried down carbon with it; this was not the case with the other metals. Antimony, it was discovered, could also be deposited from an ammoniacal and alkaline tartrate solution quite rapidly, but after it had been converted into a higher oxide by means of bromine, and its solution then mixed with tartaric acid and ammonia sufficient to render it strongly alkaline it was no longer precipitated by the current. With this difference in behavior toward the current before us we combined copper and antimony solutions in the presence of tartaric acid and ammonia, then electrolysed the same. The results we obtained show that the separation is possible and very satisfactory. We purposely varied the quantities of the two metals to render it certain that we could rely upon the method even under varying conditions.

	Copper present in grams.	Antimony present in grams.	Current in cc. O-H gas per minute.	Total dilution, cc.	Copper found in grams.
1.	0.1341	0.1087	1.4	175	0.1341
2.	0.1341	0.1449	1.4	175	0.1343
3.	0.1341	0.2898	0.8	175	0.1344
4.	0.1341	0.1449	1.0	175	0.1340
5.	0.0134	0.1449	1.0	175	0.0142
6.	0.0268	0.1449	1.0	175	0.0274
7.	0.0670	0.1449	1.0	175	0.0670
8.	0.1341	0.1449	1.0	175	0.1341
9.	0.1341	0.1449	1.0	175	0.1341

The volume of ammonia present in each of these determinations equaled fifteen cc. (sp. gr. 0.932). The tartaric acid varied from three to four grams. The dishes in which the copper was precipitated ranged in weight from sixty to seventy grams. An examination of the deposited metal showed no antimony. It may be remarked that the strength of current maintained in these determinations was that indicated by the voltameter before the introduction of the electrolyte into the circuit of decomposition.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF PENNSYLVANIA, APRIL 17, 1893.

ON THE GRAVIMETRIC DETERMINATION OF THE PENTAGLYCOSES.

BY E. R. Flint, Ph.D.

On page 68 (Vol. VII, February, 1893) of this journal is an article by W. H. Krug on the gravimetric estimation of furfurol hydrazone, in which he gives a resumé of the improvements made since the first practical method was worked out by Tollens and Günther. Many of the improvements mentioned were made by myself, in the winter of 1891-92, when, in connection with Prof. Tollens, I made a very careful investigation of the methods which had been proposed up to that time and suggested most of the changes in the method of de Chalmot which the author mentions, without giving me credit for the same. As a result of the above investigation I proposed a method following essentially that of de Chalmot, but embodying the improvements made,

which, as the results of several analyses made by myself will show, will compare favorably in accuracy and rapidity with many of the other analytical methods used in plant analysis.

As the results have never, to my knowledge, been published in this country,[1] and as the author of the above mentioned article has possibly failed to see the same in connection with my name, I should like to state, in a few words, the method I finally adopted, together with some analytical results obtained. Three methods have been proposed, namely, the titration methods of Günther and Stone, and the gravimetric method of de Chalmot. In comparing these, I soon discovered that the titration methods generally gave higher results, resting evidently upon the following cause. The majority of articles to be tested (plants and fodder articles) contain more or less glucosides, frequently to a very high per cent. These, by the distillation with acid, yield, as is well known, more or less laevulinic acid, aceton, and similar compounds, the presence of which I proved in the distillate in several instances. These compounds combine with phenylhydrazin, but in fairly dilute solutions, at least, do not give a precipitate. This fact gives all the titration methods an inaccuracy which the gravimetric method, by precipitation, escapes. The extent of this effect is shown in the following figures;[2]

Furfurol, gm.	To which was added	Phenylhydrazin sol. required, cc.	One cc. = gm. furfurol.
0.2046	......	7.1	0.02883
0.2046	0.2 gm. aceton	8.4	0.02451
0.2046	0.5 " "	10.2	0.02006
0.2046	0.2 " laevulinic acid	8.8	0.02326
0.2046	0.5 " " "	10.5	0.01949

These tests show a considerable difference, more phenylhydrazin solution being required as more laevulinic acid or aceton was present.

Turning to the titration method of de Chalmot, some improvements were made in the manipulation as proposed by him. He recommends that the distillate after adding the phenylhydrazin should be stirred five minutes and stand half an hour. By con-

[1] They may be found in detail on page 2912 of the *Ber. d. chem. Ges.*, 25, 1892.
[2] The phenylhydrazin solution for titration was made according to Günther—five gms. phenylhydrazin, three gms. glacial acetic acid, filled to 100 cc. with water.

tinuous stirring during the half hour, the separation is much more perfect, the supernatant liquid and subsequent filtrate being in all cases perfectly clear for some time (a final clouding of the filtrate is evidently a separation or possible decomposition, which all solutions of phenylhydrazin appear to undergo). That portion of the precipitate adhering to the walls of the vessel and the stirring rod may be readily washed off by aid of a feather.

By substituting glass wool in place of asbestos in the filtering tubes, the filtration is rapid and complete. I also found it advantageous to introduce calcium carbonate tubes between the sulfuric acid flasks for drying the air, and the filtering tubes, while drying the precipitate, to intercept any sulfuric acid which may be mechanically drawn up by the current of air. A manometer should also be placed between the filtering tubes and the pump to regulate the suction.

The amount of salt present (from neutralizing the hydrochloric acid distillate with sodium carbonate) influences the result to some extent. To remedy this I proposed filling the distillate always to 400 cc. with hydrochloric acid of 1.06 sp. gr. (the same strength as that used in the distillation), before neutralizing with sodium carbonate, and under these conditions the factor for reducing the hydrazone to furfurol or the pentose, was determined, thus eliminating this source of error.

I was less fortunate in finding a means to obviate the error caused by the presence of more or less carbohydrates, which is shown by the following figures from experiments with starch mixed with pure xylose:

Xylose.	Starch.	Hyrdrazone.	=Furfurol.
1 gm.	....	0.9821 gm.	0.5284 gm.
1 "	....	0.9844 "	0.5296 "
1 "	1 gm.	0.9526 "	0.5125 "
1 "	1 "	0.9555 "	0.5141 "
1 "	2 "	0.9281 "	0.4993 "
1 "	2 "	0.9317 "	0.5013 "
1 "	3 "	0.9033 "	0.4860 "
1 "	3 "	0.9089 "	0.4890 "

Thus the presence of three gms. of starch gave about four per cent. furfurol too little. Experiments with a mixture of xylose with cane sugar and with cellulose (filter paper) gave similar

results. We have thus an unavoidable inaccuracy attached to all methods for the determination of the pentose resting on the distillation with hydrochloric acid. It may be brought to a minimum, however, by using small amounts of the substance to be tested, preferably two gms. rather than five gms.

The factors for the conversion of the hydrazone to furfurol, xylose, arabinose, or pentose were recalculated from a large series of careful tests with pure xylose and arabinose, and are as follows:

$$Furfurol = Hydrazone \times 0.538.$$
$$Arabinose = \text{``} \quad \times 1.229 + 0.0177.$$
$$Xylose = \text{``} \quad \times 1.031 - 0.001.$$
$$Pentose = \text{``} \quad \times 1.13 + 0.0083.$$

The accuracy of the above formulas is shown in their application in the following tests with pure xylose and arabinose:

Arabinose used.	Hydrazone.	Arabinose found. (Hydrazone × 1.229 + 0.0177.)
0.1 gms.	0.0522 gms.	0.0819 gms.
0.25 "	0.1891 "	0.2501 "
0.50 "	0.3905 "	0.4976 "
0.75 "	0.5756 "	0.7251 "
1.0 "	0.8139 "	1.0179 "
1.5 "	1.2146 "	1.5104 "
2.0 "	1.6144 "	2.0018 "
2.5 "	2.0205 "	2.5008 "

Xylose used.	Hydrazone.	Xylose found. (Hydrazone × 1.031 − 0.001.)
0.1 gms.	0.0822 gms.	0.0837 gms.
0.25 "	0.2434 "	0.2500 "
0.5 "	0.4928 "	0.5071 "
0.75 "	0.7274 "	0.7489 "
1. "	0.9832 "	2.0127 "
1.5 "	1.4691 "	1.5136 "
2. "	1.9415 "	2.0007 "
2.5 "	2.4248 "	2.4990 "

As the mother substances of the hexaglycose (starch, cellulose, etc.) differ from the latter in their molecular constitution by having one water less, we may naturally accept the same difference in the constitution of the pentosan (gums, etc.) occurring in the vegetable world, and the pentose, the relation of the two classes of compounds being evidently analogous. Thus to

reduce xylose to xylan and arabinose to araban, or the pentose to the pentosan, we may make the proportion

$$C_5H_{10}O_5 : C_5H_8O_4 = 150 : 132 = 1 : 0.88$$

Thus by multiplying the per cent. of pentose by 0.88 we get the per cent. of pentosan in the substance tested.

The results of some tests made with the above method are as follows (calculated to dry matter):

	Furfurol, per cent.	Xylose, per cent.	Arabinose, per cent.	Pentose, per cent.	Pentosan, per cent.
Fir wood	4.87	9.32	......	......	8.20
Beech wood	18.20	35.08	......	......	30.87
Wheat straw	12.99	24.89	......	......	21.90
Brewers' grain (spent)	16.03	30.68	......	......	27.00
Corn cobs	18.36	35.16	......	......	30.94
Sulfite cellulose	2.89	......	......	6.25	5.50
Soda cellulose	2.90	......	......	6.35	5.59
Cherry gum	25.41	......	59.05	......	51.96
Gum tragacanth	16.17	......	37.28	......	32.81
Agar-Agar	0.88	......	......	2.02	1.78
Wood gum, No. 1	38.78	74.27	......	......	65.36
" " No. 2	46.90	89.83	......	......	79.05
" " No. 3	48.08	92.07	......	......	92.02
" " No. 4	33.30	63.73	......	......	56.08

RAPID METHOD FOR THE ESTIMATION OF PHOSPHORUS IN TITANIFEROUS IRON ORES.

BY CHARLES BASKERVILLE.

Having quite a number of analyses of titaniferous iron ores to make, and desiring to avoid the exceedingly long and tedious process ordinarily used for the determination of phosphorus in such, I was led to carry on some experiments by which I could shorten the method. The fact that the impure titanic oxid precipitated from a potassium bisulfate fusion· is freed from the contaminating phosphoric acid by a fusion with sodium carbonate and leaching,' caused me to believe that the phosphorus could be leached direct from the ore just after fusion.

This method has been tried with success as may be seen from the following results obtained from three ores varying in their

percentages of iron and titanium and phosphorus—one contained a high percentage of alumina:

A (No. 123) TiO_2, 2.40 per cent.; Fe, 31.92 per cent.;
Al_2O_3, 18.47 per cent.

Phosphorus.

1 .... 0.027 per cent., 3 gms. used.
2 .... 0.025   "   2   "   "
3 .... 0.021   "   2   "   "
4 .... 0.024   "   3   "   "

No. 1 was carried out according to the molybdate method, weighing the phosphoric acid as magnesium pyrophosphate.[2] Nos. 2, 3, and 4 were leached.

B (No. 165) TiO_2, 3.20 per cent.; Fe, 20.64 per cent.

Phosphorus.

5 .... 0.016 per cent., 4 gms. used.
6 .... 0.018   "   2   "   "

C (No. 124) TiO_2, 14.90 per cent.; Fe, 36.00 per cent.

Phosphorus.

7 .... 0.0648 per cent., 1 gm. used.
8 .... 0.0648   "   2 gms. "
9 .... 0.0585   "   2   "   "
10 ....,........ 0.0603   "   2   "   "
11 .... 0.0648   "   2   "   "
12 .... 0.0675   "   2   "   "
13 .... 0.0659   "   3   "   "
14 .... 0.0579   "   2   "   "

All analyses made are reported save three which were lost. No. 9 was carried out in sixty-five minutes without the use of suction, which no doubt would have lessened the time consumed, as twenty-three minutes were taken up in filtering. No. 14 was carried out by dissolving the ore in hydrochloric acid, filtering, using dilute acid for washing to prevent the titanium from running through the filter. The residue was fused with sodium carbonate, leached, and the filtrates combined. This method has previously been reported (Drown and Shimer,[3] Jennings[4]), though I was not aware of the fact until my work was finished.

The process.—Two grams of finely pulverized ore which has been dried at 100° C. by heating for two hours in an air bath,

are thoroughly mixed with about twenty grams fusing mixture
(ten parts sodium carbonate, one part potassium nitrate), and
brought to a quiet fusion in a spacious platinum crucible.   After
five minutes more heating the fusion is run well up on the sides
of the crucible, which is rapidly cooled by alternate dipping and
removing from water in a beaker.   The crucible is finally
plunged into the water, inverted, and let stand over night.   To
avoid this delay the crucible may be filled with distilled water,
held over the beaker, and boiled hard.   Repeating this ten times
the leaching was found to be quite as thorough as standing over
night.   The solution, which now amounts to about 300 cc., is
filtered and the residue washed with hot water four or five times.
Twenty-five cc. of ferric chlorid, containing about 0.1 gram of
metallic iron, is then added.   The solution is acidified with hydro-
chloric acid, brought to a boil, and precipitated with ammonia, and
the precipitate is washed twice with hot water after filtering.
The precipitated hydrate and phosphate of iron is then taken up
in forty cc. hot concentrated nitric acid (1.43); twenty-five cc.
strong ammonia are then added and the whole thoroughly mixed.
The solution in an Erlenmeyer flask of about 300 cc. capacity is
heated up, or cooled down, to 85° C. and thirty cc. of molybdate
solution added, washing off the bulb of the thermometer in pour-
ing it in.   The flask with a velvet cork is wrapped in a towel and
shaken hard for one minute, placed in a warm place, and allowed
to settle for five minutes, then filtered.   The phosphorus is deter-
mined by titrating the yellow phospho-molybdate precipitate
according to Manby[5] as modified by Handy.[6]

NOTES.

[1] Drown and Shimer, *Am. Chem. J.*, **4**, 6, and Streit and Franz, *Ztschr. anal. Chem.*, **9**, 388.

[2] Blair, 1892 edition, p. 223.

[3] Drown and Shimer, *Am. Chem. J.*, **4**, 2.

[4] Jennings, *Engineering and Mining Journal*, **45**, 26.

[5] This Journal, **6**, 82.

[6] This Journal, **6**, 204.

CHEMICAL LABORATORY,
UNIVERSITY OF NORTH CAROLINA.

AN ARRANGEMENT FOR HYDROGEN SULFID.[1]

By G. A. Goyder.

A modified form of hydrogen sulfid apparatus has been fitted up, both in the assay and students' laboratory, and as it has been found to work very economically, and with less trouble
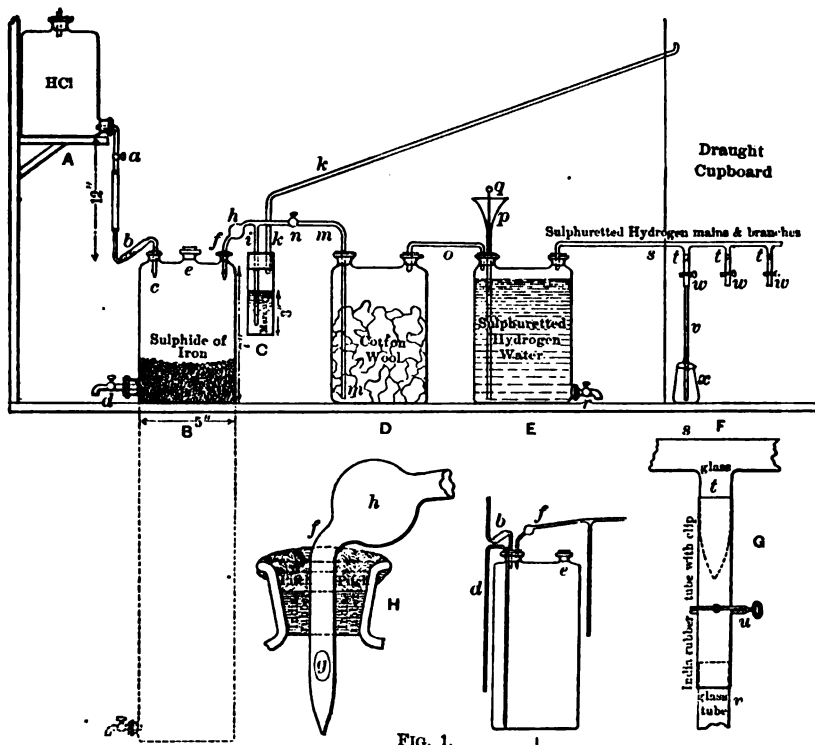
FIG. 1.

than those previously in use, and with a minimum of smell, a description of it is appended.

CONSTRUCTION.

The construction of the apparatus may be readily seen from Fig. 1. The stopper in A should fit loosely. The tap a may be replaced by a pinchcock. The valve b may be made by bending a ten cc. or fifteen cc. pipette, and it is joined to a by a piece of

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rather stout India rubber tubing, the ends being tightly tied over the glass. This remark applies to all the India rubber tube connections used. The lower end of *b* is drawn out, as at *c*, so that only a very thin stream of acid can run through it. *b* is fixed in the neck of B by means of a short India rubber stopper.

B is most conveniently made from a Woulff's bottle, with three necks at the top and one neck near the bottom (a bottle with two necks at the top only may, however, be used, by having an India rubber stopper perforated with three holes, through which pass *b f*, and a siphon reaching to the bottom instead of the tap *d*. See I). A bottle three feet high by about five inches in diameter, as shown by the dotted line, would be much preferable to the one used, which is about seven inches high by five inches diameter, but the former is not at present procurable.

e, the middle neck of B, is used for inserting the iron sulfid, and should be easily accessible and fitted with an India rubber stopper tied down.

The third neck of B is fitted with a tube, as shown at H enlarged. This may be done by drawing out a glass tube to a capillary and sealing the end; the bulb *h* is then blown out; the tube is then heated at *g* over the blowpipe flame, while blowing into the other end of the tube until a hole is made, the edges of which are flattened down by the blowpipe; the sealed end is then cut off, leaving a small opening. *f* is fitted into the neck of B by means of an India rubber cork pressed down about half an inch, and the cup thus formed filled with melted pitch. The same method is used for the other necks fitted with tubes, and in case of a breakage the stoppers can be removed after warming the neck carefully with a Bunsen flame.

The funnel *p* in E is kept closed by a glass rod tipped with India rubber tubing.

The hydrogen sulfid branch pipes for students are made by joining glass **T** pieces, as seen enlarged at G. The down pipe *t* is drawn out to a thick capillary and cut off, and the size of the capillary adjusted by blowing through the other end of the tube, after fitting a glass tube to it with India rubber tubing, until only a slow stream of air passes when blowing with moderate pressure.

The arrangement of the different bottles can of course be modified by varying the lengths of the connecting tubes to suit the space available.

In setting up the apparatus care should be taken that fresh acid may be poured into A, fresh iron sulfid put into B, more water poured into E, and spent acid drawn off through d, without disconnecting any of the parts or moving any of the bottles.

A is filled with dilute hydrochloric acid (1 : 1).

b. As much mercury is put in b as will fill at least four inches of the upright tube.

B. Some small marbles are placed at the bottom of B to prevent d being choked by iron sulfid, and the rest of the bottle is filled with iron sulfid.

C contains three inches of mercury.

D is filled with cotton wool.

E is filled with distilled water.

The bulb h in f is not essential.

Taps may be used instead of the clips at tt'.

ACTION.

The apparatus being set up as described, the tap n being closed, on opening the tap a the acid flows gently into B through b, and hydrogen sulfid is generated. As soon as the pressure rises in B the mercury in b is driven back and stops the flow of acid. Should much acid have entered B the pressure may increase until the mercury is depressed to the bottom of i in C, when some gas escapes through k into the draught cupboard. On opening n the gas passes through g into f; thence through D into E, where it is slowly absorbed by the water, which soon becomes saturated. The beaker of solution x is then connected with t by the tube v, and the clip on w opened, when a slow and regular current of hydrogen sulfid passes until the clip is again replaced on w. Similar beakers may of course be attached to t', t'', etc.

Hydrogen sulfid water may be drawn from E by r as required.

Fresh acid is poured into A as required.

The iron sulfid in B should be replaced, before it gets low, through e, a being turned off meanwhile.

More water may be added to E through the funnel p, the tap n being turned off before taking out plug q.

The tap a can be left open, except when putting iron sulfid into B; and the tap n need only be closed when the apparatus is not required, as the large size of D and the water in E in a great measure prevent the blow off of hydrogen sulfid through k when a rapid supply of gas is suddenly stopped.

The mercury in the valve b remains quite clear and bright; that in the safety blow off tube c has become a little blackened after six months' use, but its action is quite unimpaired.

The hydrogen sulfid water in E keeps quite clear and bright, and free from any trace of iron.

The tube f has proved very effectual in preventing the passage of any liquid with the gas, even when the evolution of gas is very rapid. A similar plan has been tried in distilling off the alkaline liquid from a Kjeldahl determination of nitrogen, the end of the tin condenser being drawn out to about three-sixteenths of an inch inside diameter, and a slot cut at g (as in H). There was, however, no bulb at h. In working this it was found that the tip at the bottom was always closed by a drop of water, and all the vapor passed through g into the condenser. The distillate from a strongly alkaline solution, kept rapidly boiling, in a test experiment was quite neutral.

A modified form of this apparatus has also been tried for generating hydrogen and carbonic acid gas when a
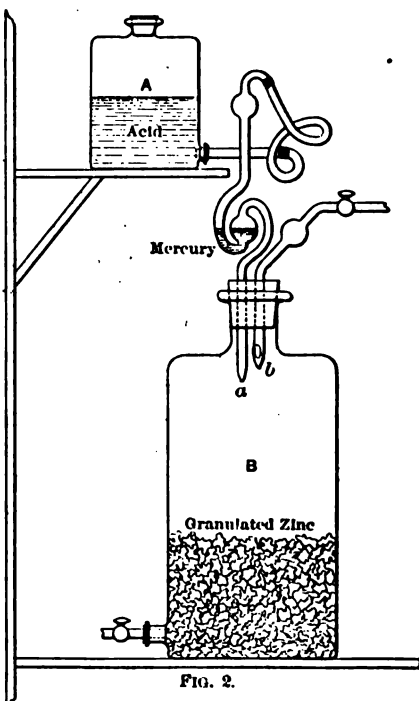
FIG. 2.

constant supply was required for some time, and it was found that the supply could be regulated much more accurately than with the apparatus generally used. Fig. 2 illustrates this apparatus, which requires no further description except that it is well to have the bottle B long and narrow and A short and wide, and the tip of the tube *a* should be below the tip *b*. The bottle A can, of course, be raised or lowered as required, being connected to B by India rubber tubing.

THE LIMITS OF ACCURACY OF GOLD BULLION ASSAYING, AND THE LOSSES OF GOLD INCIDENTAL TO IT.[1]

BY T. K. ROSE.

Some of the causes of the errors in the assay of gold bullion by the ordinary method are referred to, and it is shown that:

1. A higher degree of accuracy is attained if the weighings be made with the precautions recommended by Kohlrausch and others on a balance indicating differences of 0.01 per 1000 ($\frac{1}{2}$ gm.), instead of 0.05 per 1000, which is the smallest difference shown on ordinary assay balances.

2. Differences either in the amount of copper present to the extent of only 16 parts per 1000 of alloy, or in the amount of silver added to the extent of three per cent., produce alterations in the "surcharge" of about 0.05 and 0.1 per 1000 respectively; the "surcharge" being the difference in weight between the gold existent in the assay piece originally taken and the cornet finally obtained; it is the algebraical sum of the gold lost and the silver remaining undissolved by the acids. The reduction in the surcharge due to the presence of antimony, zinc, tellurium, iron, or nickel is also given.

It therefore follows that, in order to ensure accuracy, check assays must be made on alloys of the same composition as those under examination.

3. The want of uniformity of temperature ordinarily prevailing in the muffle furnace during cupellation causes variations in the surcharge. The temperatures of the different parts of a muffle

at the Royal Mint were taken during cupellation by a thermo-electric pyrometer—consisting of a platinum and rhodioplatinum couple—on three occasions, from which it appears that the mean temperature of the muffle was 1063.7°. At this temperature, a rise of about five degrees is found to be accompanied by a reduction in the surcharge of about 0.01 per 1000.

If attention be paid to these points, the gold in bullion of a high degree of purity can be determined within a range of ±0.02 per 1000, the limits of accuracy having been previously considered to be ±0.10 per 1000. This extreme degree of accuracy is only possible if the check gold be pure.

In the second part of the paper, the losses of gold in bullion assaying are estimated. They are due to (1) absorption by the cupel; (2) volatilization in the muffle; (3) dissolution in the parting acid.

The results of a number of assays are given, the gold having been in each case recovered from the cupels and acids, and, after the gold so recovered has been allowed for, the loss by volatilization is estimated by difference. The losses, in parts per 1000, observed in the assay of standard gold (916.6 fine) were:

	A.	B.	C.
In cupel	0.513	0.36	0.51
" first acid	?	0.01	0.03
" second acid	0.012	0.02	0.04
Volatilized	0.075	0.05	0.06
Total loss	0.60	0.44	0.64

A and B are means of four, and C a mean of three, determinations. Other results are also given.

The determination of the amount of gold volatilized is only approximate, as the result obtained represents the algebraical sum of the errors in several estimations added to the true amount. However, it probably usually lies between 0.05 and 0.1 per 1000.

The volatilization of gold.—The loss of gold involved in the fusion of the pure metal and its alloys was investigated by subjecting small test pieces of from 0.5 to 2 gms. in weight to a high temperature under varying conditions on bone-ash cupels placed in a muffle. The work may be considered to be a continuation of the researches of James Napier (*J. Chem. Soc.*, **10,** **229;**

11, 171). The temperatures varied from 1045° to 1300°, and were measured by either a platinum and rhodioplatinum couple or the optical pyrometer devised by M. le Chatelier. The losses of gold could not be measured by the alteration of the test pieces in the muffle owing to absorption of gases, which sensibly augments the weight of the gold buttons. The true loss was found by assaying the buttons after fusion.

A considerable number of results are quoted. The chief points of interest to which attention is drawn are that:

1. An increase in the loss of gold takes place when the temperature is high, pure gold losing four times as much at 1245° as at 1090°.

2. A large amount of gold is volatilized in an atmosphere mainly consisting of carbonic oxid, while a small amount is lost in coal gas.

3. A comparatively small amount of gold is carried away by the more volatile metals, copper appearing to exert an exceptional action; metals which are easily volatilized do not appear to be completely driven off by the highest temperatures attained in the experiments.

4. A large proportion of gold is lost in the case of alloys which form flat buttons on the cupel, and, conversely, a small proportion is lost from spherical ones, although the surface actually exposed is greater in the latter case than in the former. A current of air or gas passing over the buttons does not seem to increase the loss, provided the surface of the molten metal remains at rest. These results point to the conclusion that the conditions which lower the surface tension of the gold button simultaneously raise the vapor pressure of the gold.

DISCUSSION.

Professor Roberts-Austen said that, prior to the last few weeks, he should certainly have considered that the accuracy of an assay of gold was comprised within a range of $\pm\frac{2}{10000}$. Mr. Rose had, however, tracked the errors to their respective sources, and had shown that a still higher degree of accuracy can be attained in ordinary work. It was not a little remarkable that although Princep (one of the best assay masters who ever held that impor-

tant office) had clearly indicated in 1827 the importance of know-
ing the variations of temperature in an assay muffle, no one had
attacked the problem until Mr. Rose took it in hand.   Although
questions connected with assaying did not often come before the
Society, they were matters to which the fathers of chemistry had
given much attention.   He might remind the Society that, apart
from scientific interest, these minute questions connected with
assaying assumed considerable industrial importance.   During
his connection with the mint, extending over more than twenty
years, he had been responsible for the standard pureness of more
than 600 tons of gold, the value of which was over eighty millions
sterling.   As regards the number of assays made, he and his two
colleagues, the assistant assayers, had made in the past year no
fewer than 30,000 assays of gold, and they had every reason to
believe that their average accuracy was $\frac{1}{10000}$ part.

ON PHENOLPHTHALEIN AND METHYLORANGE
AS INDICATORS.[1]

BY MARY BIDWELL BREED.

In using phenolphthalein as an indicator in alkalimetry, there
are certain precautions necessary that have not been sufficiently
insisted upon in the literature of the subject.   The following
experience, however, will show the necessity for great care in
its use.

During the standardization of a hydrochloric acid solution
against normal caustic potash, phenolphthalein and methylorange
were both used as indicators: and it was observed that, while
with methylorange 20 cc. of the acid required only an average
of 19.443 cc. of the alkali for neutralization, with phenolphthalein
the same amount of acid required an average of 19.765 cc. of
alkali, a difference which would introduce a considerable error.
The same results were obtained with phenolphthalein, even when
the solution was heated to boiling, and so it was believed that
carbon dioxid could not be the cause of the discrepancy.   That
the source of the difficulty lay with the phenolphthalein, and not

with the methylorange, seemed probable from the fact that it took more alkali to bring the color of phenolphthalein than to discharge that of methylorange; and also from the fact that, while the amounts of alkali used with the former varied from 19.65 cc. to 19.8 cc., those used with the latter were practically constant, differing only by 0.025 cc. Nothing could be found in the literature of the subject that threw any light on the problem. Fresh solutions, prepared with great care, gave analogous results, and after many fruitless attempts to explain the discrepancy, it was concluded that traces of carbon dioxid, dissolved by the alkali, must after all be the source of error. This would explain matters, for acid potassium carbonate, which would be formed in the solution during titration, is neutral to phenolphthalein, but alkaline to methylorange; and, therefore, as part of the alkali had been rendered neutral to phenolphthalein, it would take more of the solution to affect that indicator than to affect methylorange. This explanation was proved to be correct by prolonged, hard boiling of the solution, when using phenolphthalein. Alkali was titrated with acid in this case, and it was found that, by boiling ten minutes or so after the end point had been apparently reached, the color could be made to reappear, and that it continued to reappear after each addition of acid until the amount of acid used was exactly equal to that used with methylorange. As the end point was approached, longer and longer periods of boiling were necessary after each drop added. A single titration never took less than an hour.

In view of this, a word of caution seems necessary. It is never safe to use phenolphthalein unless the solution is known to be absolutely free from carbon dioxid, or unless it is boiled long and thoroughly after the end point is apparently reached. As it is nearly impossible to keep a solution of caustic alkali entirely free from carbon dioxid, a titration with phenolphthalein is often as tedious as a gravimetric determination.

Phenolphthalein is probably used at present more extensively than any other indicator, but these objections make it desirable to adopt something more reliable and convenient. Methylorange is not affected by carbon dioxid, and when a sufficiently dilute solution is used, its end point is sharp. It has been found very

satisfactory for sensitiveness and accuracy, and it is therefore strongly recommended wherever it is possible to use it.

DISCUSSION.

Mr. Haines suggested that the glass beaker may have been attacked by the boiling alkaline solution, resulting in extraction of alkali from the glass, especially if the boiling was continued as long as an hour. Such action has been observed even with Bohemian glass. The glass is stated to be generally attacked as a whole. As regards phenolphthalein and methylorange he wished to call attention to the statement by R. T. Thomson, in his comprehensive papers on indicators (*Chemical News*, **47**, 123, 184, and **44**, 32, 38, 119), that phenolphthalein has five times greater delicacy or sensitiveness than methylorange. In other words, in 100 cc. of distilled water, the former requires but 0.1 cc. of excess of decinormal solution, while the latter requires 0.5 cc. of excess to produce the full change of color. In solutions of normal strength the difference is scarcely noticeable. He showed that this difference was not due to carbonic acid, but to the interference of neutral salts of sodium, potassium, and ammonium formed during titration, which affect the delicacy of methylorange, but not phenolphthalein, except in the case of salts of ammonia. Neutral salts of calcium, barium, and magnesium have the same effect upon methylorange. Mr. Haines said that in recently making some determinations, requiring the use of both of these indicators, he had found the above statement as to this difference to be correct. A fresh standard solution of sodium hydrate, made from metallic sodium and carefully protected, gave practically the same results as an old solution of ordinary sodium hydrate in white sticks. In determining alumina volumetrically in sodium aluminate by the method described by Lunge (*J. Soc. Chem. Ind.*, 1891, p. 314), in which both indicators are used and the amount of alumina is calculated from the difference of results of titration, Mr. Haines obtained results which agreed very closely with gravimetric estimations in the same solutions if the above correction for difference in delicacy of indicators was applied. Generally, methylorange is used only in a cold solution, but Lunge has shown that in estimating

alumina volumetrically with methylorange, the solution should be heated to 30° to 40° C., but not exceeding the latter temperature. The action in the cold solution is too slow and the alumina is apt to be underestimated. Only dilute solutions of alumina should be used.

Phenacetolin also is a more delicate indicator than methylorange, being similar in this respect to phenolphthalein. In estimating calcium, magnesium, and sodium carbonates, as in Hehner's method of determining hardness of waters, Mr. Haines has found, as others have also, that phenacetolin is preferable to methylorange, but in this case the former must be used hot, the latter cold. He finds that the alcoholic solution of phenacetolin keeps very much better if it is not filtered from the insoluble residue found in the article as sold.

Mr. Haines has also experienced some difficulty in obtaining the true methylorange (helianthin). Sutton incorrectly describes it as of a bright orange red color ; Allen states it is orange yellow. An article of bright orange red color sold in this country as methylorange gave the *reverse* of the correct colors with acids and alkalis and was so wanting in delicacy as to be practically worthless.

The article recently obtained from Bullock and Crenshaw, which agrees nearly with Allen's description, he had found to be perfectly satisfactory.

Mr. Henry Pemberton, Jr., remarked that in titrating with phenolphthalein and with methylorange as indicators, different results would be obtained if the standard alkali contained alumina. This impurity is not frequently present in sodium or potassium hydrate. Even a small amount of alumina (*about* 0.002 gms.) will require when methylorange is used one cc. of $\frac{n}{10}$ acid more than when phenolphthalein is used.

In regard to titrations with phenolphthalein in the presence of ammonium salts, J. H. Long has shown[1] that correct results are obtained when the solution is kept cold and a sufficient quantity of the indicator is employed.

Prof. E. S. Keiser, in reply to Mr. Haines, said that while according to R. T. Thomson, methylorange was not as sensitive

[1] *Am. Chem. J.*, 11, 84.

as phenolphthalein, other observers had found it to be more sensitive. For example, J. Wieland (*Ber. d. chem. Ges.*, **16,** 1989), found that from three to four times as much of a $\frac{1}{100}$ normal solution was required to bring about the change of color with phenolphthalein as with methylorange. That is, the phenolphthalein is less sensitive than the methylorange. Experiments made in the speaker's laboratory indicated that methylorange when used in the proper dilution was fully as sensitive as phenolphthalein. The great objection, however, to the use of phenolphthalein in ordinary titrations is its sensitiveness to carbon dioxid, and that it is neutral to acid carbonates. For example, R. B. Warder (*Am. Chem. J.*, **3,** 55) has shown that alkaline solutions of this indicator can be decolorized by shaking them with air, and that by simply breathing upon the red liquid the color is discharged. The phenolphthalein is not colored by acid carbonates. Mr. Haines would find in the paper by R. T. Thomson, to which he refers, that that author distinctly states that when alkaline hydroxids containing alkaline carbonates are titrated and phenolphthalein is used as indicator, the color disappears when the hydroxid is neutralized and the carbonate changed to acid carbonate. That if the solution is then boiled the color reappears, because the acid carbonate is decomposed, and more acid must be added and the titration continued until the color no longer appears in the boiling solution.

As it is almost impossible to prevent standard alkali solutions from absorbing carbon dioxid from the air, it is evident that the strength of such solutions will constantly change if the determinations are made with phenolphthalein as the indicator. On the other hand, if the titrations are made with methylorange as the indicator the results are in no way influenced by the amount of carbon dioxid that has been absorbed. Hence, in all ordinary work it is advisable to use methylorange.

THE RIVER NILE.

BY H. DROOP RICHMOND, LATE SECOND CHEMIST TO THE EGYPTIAN GOVERNMENT.

I. INTRODUCTION.

The river Nile, the water-way of Egypt, is chiefly fed by the great equatorial rains; it drains an enormous area of northeast and northeast-central Africa, and reaches from about 4° south latitude to 31° north latitude, and runs, broadly speaking, south to north.

The Nile proper does not exist before Khartoum is reached; south of this it is composed of (a) the White Nile, (b) the Blue Nile, into which runs just above Berber the (c) Atbara or Black Nile. These names do not indicate the color of the water, but rather the intensity of the color due to suspended matter, and afford an instance of the figurativeness of Oriental language.

(a) The White Nile has its sources in the three great lakes, the Victoria, Albert, and Albert Edward Nyanzas, and receives the waters chiefly from the northern and eastern sides of the snow-clad mountains by means of many small tributaries; it passes for some distance after leaving the lakes through a marshy country, and here takes up a considerable quantity of vegetable matter, to which the green color noticed just before the flood is due; some of its tributaries, notably the Saubat, contain carbonate of calcium in suspension, and to this its name of White Nile has been ascribed by many, though it owes its name more to its comparative cleanness and freedom from suspended matter.

(b) The Blue Nile drains the southern side, (c) the Atbara the northern side, of the Abyssinian mountains; they are both of the same character, and contain large quantities of mud in suspension, especially in flood time, and to this, which imparts a dark red-brown color to the water, are the names Blue and Black Nile due.

All three rivers rise in the spring, the White Nile to a less extent than the others; except during this rise the water of the Blue Nile is small in amount compared with that in the White, which has large reservoirs in the lakes; this comparative constancy of the White Nile prevents the Nile in Egypt from sinking

into insignificance.   The rise of the White Nile always takes place before that of the Blue, and the first symptom of this is the carrying down of its more or less stagnant waters of a greenish hue, which reach Cairo about the months of June or July, and cause the Nile water to be at its worst at that period; about a month afterwards the Blue Nile rises enormously and carries down with it immense quantities of suspended mud, and it is to this rise that the flood of the Egyptian Nile is due.

The two rivers join at Khartoum, and run for miles side by side with a fairly sharp line of demarcation,

THE NILE

distinguished by the difference of color of the two waters; it flows thence over four "cataracts" or rather rocky parts to Wady

Halfa, where it enters Egypt, and at which point the present re-
search commenced ; near Wady Halfa is the second and largest
cataract, and from then it continues to the first cataract at As-
souan, where is a Nilometer or *gauge* of the height of the river,
from the readings of which the state of the flood is *gauged*; flowing
past Edfoo, where is another Nilometer, (now disused, but of great
interest as having furnished the clue to the length of the Nile
"pic" or "drâa," the measure of the ancient Egyptians; c. f.
Moukhtar Pasha, *Etudes sur les Mesures Egyptiennes*, Cairo,
1890), and Keneh, it reaches Assiout, where the Ibrahimieh canal
leaves the river, to become at Deyrout the Bahr Yousef, or
Yousefy River, which waters the Fayoum, and ends in the Birket-
el-Kûm, often called Lake Moeris, but probably not the lost Lake
Moeris, which was farther south. From Assiout, it flows past
Minieh and Beni-Souef to Cairo, where on the southern end of
the Island of Rodah is another Nilometer, anciently used to show
the state of the flood, but whose indications are now too much
affected by the drawing off of water in Upper Egypt for irriga-
tion purposes to be reliable. At Cairo the Ismailieh Canal
branches off to Ismailia and falls into the Gulf of Suez near the
town of Suez. Nineteen miles beyond Cairo is the Barrage, a
great bridge whose arches can be closed, converting it into a
dam and raising the water level so that the irrigation canals can
be supplied. At the Barrage it divides into the Damietta branch,
which empties into the Mediterranean at Damietta, and the
Rosetta branch, dividing into the Mahmoudieh canal, which has
its exit at Alexandria, and the Raschidieh canal, which dis-
charges at Rosetta; a fifth branch anciently flowed through
Lake Menzaleh. From these branches the Delta is supplied by
numerous smaller canals. Along the north coast are Lakes
Mareotis (filled by the British from the sea at the commencement
of the century), Edko, Bourlos, etc., which are highly charged
with sodium chlorid; waters of this description occur also at
Shaloof and other places near the Suez Canal (c. f. Richmond
and Opp, *J. Soc. Chem. Ind.*, 9, 1108, and Richmond, *Analyst*,
17, 163); the water from these lakes finds its way into the lower
branches of the Nile and somewhat alters its character. The
waters of the Bahr Yousef are also affected in a similar manner.

II. THE NILE CHEMICALLY CONSIDERED AS THE WATER SUPPLY OF EGYPT.

The first chemical study was made in 1874-5 by the late Dr. Letheby ; he analyzed twelve monthly samples of the water taken at Boulak, sent to him by the Public Works Department ; an extract of his analyses is given in Table I ; he also made a mineral analysis of each sample.

TABLE I. ANALYSES BY DR. LETHEBY IN 1874-75.

Date.	Height of Nile.	Total solids.	Suspended matter.	Chlorin.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	Oxygen absorbed.	Coefficient of purity.
Jan. 23, 1875	15.00	14.47	16.74	0.24	0.0087	0.0143	Trace	0.257	67.4
Feb. 12, 1875..............	14.71	14.67	12.57	0.25	0.0048	0.0166	"	0.317	81.0
Mar. 15, 1875	14.26	17.81	5.31	0.61	0.0036	0.0086	"	0.417	92.7
Apr. 15, 1875	13.24	18.19	6.63	0.92	0.0035	0.0107	"	0.517	104.8
May 13, 1875..............	13.02	20.47	4.77	1.74	0.0014	0.0118	"	0.625	137.1
June 8, 1874	12.59	20.30	6.91	1.64	0.0057	0.0114	"	0.300	72.5
July 10, 1874	13.76	16.39	17.84	0.85	0.0129	0.0100	"	0.211	54.8
Aug. 12, 1874	20.18	16.60	149.16	0.63	0.0043	0.0071	"	0.237	55.4
Sept. 20, 1874	22.32	19.44	54.26	0.21	0.0100	0.0171	"	0.386	96.3
Oct. 12, 1874	22.83	15.86	37.80	0.49	0.0071	0.0143	"	0.483	112.3
Nov. 12, 1874..............	18.31	14.91	34.37	0.21	0.0064	0.0114	"	0.269	76.5
Dec. 12, 1874	16.28	13.61	28.91	0.28	0.0049	0.0108	"	0.186	49.0

In his report to the Public Works Department he drew attention to the variable character of the water, and to the amount of organic matter, and albuminoid ammonia, *which were largely in excess of those in the rivers of Europe.* This last statement laid the foundation for the general opinion that the Nile water is bad, an opinion contrary to that arrived at by the French Expedition at the begining of the century, who did not, however, make chemical examinations. Wanklyn also examined samples at the same time, and drew attention chiefly to the variation in the chlorin.

The Egyptian chemists Tanquerel 1883, (*Annuaire Egyptienne*, 1891), Pappel, 1886, and Pollard, 1888–9, (*Report of the Sanitary Administration*, 1889) also studied the Nile. Tanquerel did little more than study the mineral constituents; Pappel made twelve monthly analyses (omitting however the determination of suspended matter), but his results are so full of obvious discordances, possibly clerical errors, which a personal reference to this chemist has failed to explain, that they must be rejected

as useless; Pollard made twenty-four bi-monthly analyses of considerable value, which are given in Table II.

TABLE II. ANALYSES BY MR. POLLARD IN 1888–89.

Date.	Height of Nile.	Total solids.	Suspended matter.	Chlorin.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	Oxygen absorbed.	Coefficient of purity.
Jan. 5. 1889	14.03	13.2	13.6	0.36	...	0.010	0.10	0.32	74.5
" 19, 1889	13.93	14.0	12.8	0.50	0.002	0.010	0.13	0.33	77.0
Feb. 2, 1889	13.69	15.2	10.2	0.71	...	0.009	0.05	0.295	68.2
" 16, 1889	13.52	17.3	8.7	1.14	0.001	0.010	0.04	0.28	66.4
Mar. 2, 1889	13.47	19.5	6.0	0.14	...	0.010	0.04	0.28	66.2
" 16, 1889	13.40	20.2	5.0	1.79	0.001	0.011	0.03	0.32	75.3
Apr. 6, 1889	13.36	23.0	5.9	2.21	...	0.012	0.06	0.29	70.3
" 20, 1889	13.33	25.8	4.0	2.64	...	0.011	0.05	0.27	65.2
May 4. 1889	13.31	26.35	3.2	3.00	0.001	0.011	0.06	0.28	67.5
" 18, 1889	13.33	29.0	1.7	3.43	0.001	0.011	0.08	0.29	69.6
June 8, 1888	13.33	28.3	3.3	4.00	0.002	0.012	0.11	0.27	66.9
" 23, 1888	13.29	23.7	2.27	3.14	0.020	0.037	0.16	0.41	123.8
July 7, 1888	13.36	29.2	1.4	3.00	...	0.020	0.02	0.30	80.1
" 21, 1888	14.14	23.4	6.0	1.93	0.003	0.020	0.03	0.22	64.7
Aug. 4, 1888	14.30	20.3	...	1.50	0.008	0.017	0.03	0.28	74.7
" 20, 1888	17.43	14.3	163.1	0.57	0.005	0.007	0.38	0.30	69.9
Sept. 1, 1888	18.64	13.7	231.2	0.36	0.007	0.010	0.32	0.32	77.0
" 22, 1888	18.55	12.8	163.6	0.29	0.004	0.011	0.19	0.23	58.8
Oct. 6, 1888	17.38	12.2	105.6	0.29	0.003	0.012	0.19	0.205	55.6
" 20, 1888	16.42	12.5	...	0.26	0.001	0.010	0.22	0.22	55.3
Nov. 3, 1888	16.44	13.7	81.3	0.24	...	0.020	0.19	0.25	71.0
" 17, 1888	14.98	12.4	48.3	0.36	0.001	0.007	0.22	0.29	66.3
Dec. 8, 1888	14.39	12.6	26.2	0.29	0.001	0.006	0.17	0.22	51.1
" 22, 1888	14.19	13.6	20.9	0.29	...	0.008	0.11	0.28	64.5

Sundry French chemists have made from time to time analyses too isolated to have any value in the study of a constantly changing river like the Nile.

The whole of the foregoing analyses were made on water taken from the river at Cairo, and no attempt was made to study it at other points.

As already stated the Nile water enjoys a somewhat bad reputation, due in the first instance to Letheby, and greatly enhanced by Pappel, and to some extent Pollard; the grounds for Letheby's opinion have already been stated; Pappel's analyses are unreliable, and therefore his opinion cannot be held to have great weight, though from his position of Chief Government Chemist it was received with authority in Egypt; the latter and Pollard based their opinion on the fact that in the Nile the limits 0.004 parts per hundred thousand of albuminoid ammonia, and 0.2 parts per hundred thousand of oxygen absorbed in the Forehammer process were exceeded. As the Nile is (chemically) almost unknown,

the judging of the water by these arbitrary standards is not entirely defensible; the chemical evidence therefore that the Nile, which has been drunk by generations during six thousand years, is bad for potable purposes, is weak.

At the beginning of 1891 His Excellency, Dr. Greene Pasha, Director of the Sanitary Administration, thought it desirable to examine the water of the Nile as near its source as was possible, and he entrusted the work to my hands; with him I sketched the following plan to include analyses of (a) the Upper Nile at Wady Halfa, Assouan, Keneh, Assiout, Minieh, and Cairo; (b) the Lower Nile at Cairo, Alexandria on the Mahmoudieh canal, Rosetta on the Raschidieh canal, Damietta on the Damietta branch, Ismailia, Port Said and Suez on the Ismailieh canal, and Tantah and Zagazig on two branch canals; (c) the Bahr Yousef, at Assiout, Deyrout, and Medinet-el-Fayoum; (d) at Cairo, to study specially the monthly variations and the water of the Cairo Water Company.

The machinery of the Sanitary Administration was placed at my disposal by His Excellency, Greene Pasha, and through the kindness of Colonel Ross, Chief Inspector of Irrigation, and His Excellency, Rogers Pasha, Principal Medical Officer of the Egyptian Army, I was also able to avail myself of the aid of the Public Works and War Departments. I take this opportunity of expressing my thanks to these gentlemen and also to His Excellency, Mahmoud Pasha Sidky, Sub-Director of the Sanitary Administration, to Mohammed Bey Sidky, Chief (pro tem.) of the Technical Service Public Works Department, and to the various officials of the three departments who aided me.

All samples, except at Cairo, were taken in mid-stream by plunging a bottle to a distance of half a meter below the surface and there, after rinsing, filling it; the samples at Cairo were taken at the Kasr-el-Nil bridge by myself with the apparatus described hereafter; the water was forwarded with the least possible delay to the Khedivial Laboratory at Cairo, and the analysis immediately commenced.

The analyses are given in Tables III (Cairo), IV (Wady Halfa, Assouan, Keneh, Minieh, and Cairo), V (Alexandria, Rosetta, Damietta, Tantah, and Zagazig), VI (the same and

Cairo), VII (Ismailia, Port Said, Suez, and Cairo), VIII (Assiout, Deyrout, and Medinet-el-Fayoum), IX (Rodah, Kasr-el-Nil, and Embabeh, all near Cairo), and X (showing the effect of filtration through various media). All results are stated in parts per hundred thousand, and were obtained from the water twice filtered through paper to remove suspended matter; this proceeding has some objections, shown in Table X, but as it had been adopted by my predecessors I continued it; all results are, however, comparable (with exceptions mentioned hereafter).

TABLE III. ANALYSES AT CAIRO DURING 1891.

Date.	Height of Nile.	Total solids.	Suspended matter.	Chlorin.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.
Mar. 25, 1891.......	13.82	17.96	3.84	1.01	0.001	0.025	Trace	0.081	0.186	60.0
Apr. 28, 1891	13.98	23.12	4.52	2.09	0.007	0.038	"	0.063	0.160	68.0
May 26, 1891........	13.82	19.64	1.44	2.91	0.003	0.019	"	0.124	0.264	70.8
June 29, 1891	14.23	15.84	6.60	1.41	0.002	0.043	"	0.166	0.289	105.5
July 25, 1891	14.48	17.16	31.32	0.64	Trace	0.016	0.03	0.089	0.145	48.2
Aug. 28, 1891	18.71	16.20	188.64	0.66	0.002	0.012	0.01	0.084	0.137	42.9
Sept. 31, 1891.......	19.13	13.12	160.44	0.56	0.002	0.008	Trace	0.074	0.124	35.6

TABLE IV. ANALYSES AT CAIRO (CA.), MINIEH (MI.), ASSIOUT (AT.), KENEH (KE.), ASSOUAN (AN.), AND WADY HALFA (W. H.).

Date.	Place.	Total solids.	Chlorin.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.	Coefficient of P. corrected.
May	Ca.	19.64	2.91	0.003	0.019	Trace	0.124	0.264	70.8	70.8
"	Mi.	99.56	39.50	0.004	0.015	2.1	0.119	0.212	...	...
"	At.	19.96	2.45	0.012	0.039	0.09	0.148	0.267	98.1	98.1
"	Ke.	21.08	2.00	0.004	0.028	0.08	0.138	0.257	82.5	115.5
"	An.	...	...	...	...	...	...	...	...	...
"	W. H.	18.96	1.82	0.001	0.014	Trace	0.063	0.114	38.2	76.4
June	Ca.	15.84	1.41	0.002	0.043	"	0.166	0.289	105.5	105.5
"	Mi.	18.24	1.36	0.006	0.034	0.18	0.097	0.163	71.8	...
"	At.	14.60	1.32	0.073	0.059	None	0.164	0.372	143.6	143.6
"	Ke.	14.24	1.14	0.116	0.043	"	0.121	0.248	115.2	161.3
"	An.	14.64	1.09	0.134	0.031	"	0.104	0.208	99.4	161.0
"	W. H.	...	...	...	...	...	...	...	...	...
July	Ca.	17.16	0.64	Trace	0.016	0.03	0.089	0.145	48.4	48.4
"	Mi.	18.32	0.86	0.011	0.015	0.25	0.091	0.172	53.8	...
"	At.	16.36	0.68	Trace	0.010	0.02	0.089	0.145	42.4	42.4
"	Ke.	15.44	0.64	"	0.017	0.02	0.103	0.187	56.4	79.0
"	An.	13.84	0.59	"	0.010	Trace	0.094	0.154	43.8	70.1
"	W. H.	13.20	0.44	"	0.013	"	0.090	0.181	49.1	98.2
August	Ca.	16.20	0.66	0.002	0.012	0.01	0.084	0.137	42.9	42.9
"	Mi.	...	...	...	...	...	...	...	...	...
"	At.	13.60	0.51	0.005	0.024	Trace	0.075	0.198	60.8	60.8
"	Ke.	...	...	...	...	...	...	...	...	...
"	An.	13.20	0.44	Trace	0.013	Trace	0.057	0.139	38.3	61.3
"	W. H.	11.68	0.32	0.001	0.009	"	0.075	0.159	40.1	80.2

TABLE V.   ANALYSES AT.ALEXANDRIA, ROSETTA, DAMIETTA, TANTAH,
AND ZAGAZIG.

Date.	Place.	Total solids.	Chlorin.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.
May 17, 1891.	Alexandria.	24.60	2.91	0.004	0.026	0.02	0.112	0.258	75.1
June 19, 1891.	"	24.36	2.68	0.001	0.024	Trace	0.096	0.175	60.9
July 16, 1891.	"	21.04	1.73	0.002	0.018	"	0.072	0.186	46.1
May 20, 1891.	Rosetta.	20.48	2.00	0.012	0.028	0.04	0.128	0.257	81.9
Aug. 20, 1891.	"	...	...	0.001	0.015	Trace	0.062	0.132	40.8
May 15, 1891.	Damietta.	30.36	5.18	0.020	0.040	0.07	0.095	0.161	49.1
June 20, 1891.	"	46.76	11.36	0.006	0.023	Trace	0.069	0.139	36.1
July 16, 1891.	"	30.86	12.86	0.002	0.010	0.09	0.080	0.152	47.4
Aug. 16, 1891.	"	137.68	69.1	0.009	0.014	None	0.112	0.271	73.3
May 24, 1891.	Tantah.	22.73	2.77	0.009	0.022	"	0.112	0.271	73.3
July 12, 1891.	"	17.32	1.23	0.001	0.013	0.06	0.067	0.137	40.6
June 10, 1891.	Zagazig.	23.96	2.64	0.010	0.013	Trace	0.064	0.109	38.7
July 14, 1891.	"	17.84	1.14	0.001	0.020	0.05	0.065	0.133	46.7
Aug. 10, 1891.	"	16.88	0.87	0.001	0.010	0.02	0.062	0.134	36.1

TABLE VI.   AVERAGES OF TABLE V.
(Differences in total solids, corrected for chlorin.)

Place.	Total solids.	Chlorin.	Coefficient of purity.
Cairo	18.94	1.51	73.1
Alexandria............	23.33	2.44	60.8
Difference	+2.84	+0.93	—12.3
Cairo	18.39	1.34	67.1
Damietta	63.90	24.62	58.9
Difference	+6.71	+23.28	—8.2
Cairo	18.39	1.34	67.1
Tantah	20.02	2.00	55.9
Difference	+0.53	+0.66	—12.2
Cairo	17.21	1.65	60.8
Zagazig	19.55	1.55	40.5
Difference	+2.50	—0.10	—20.3

TABLE VII.   ANALYSES AT CAIRO, ISMAILIA, PORT SAID, AND SUEZ.

Date.	Place.	Total solids.	Chlorin.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.
April–May	Cairo.	23.12	2.09	0.007	0.038	Trace	0.063	0.160	68.0
" "	Ismailia.	25.50	2.82	0.009	0.024	0.05	0.121	0.274	77.5
May–June	Cairo.	19.64	2.91	0.003	0.019	Trace	0.124	0.264	70.8
" "	Ismailia.	19.96	2.77	0.002	0.024	0.18	0.999	0.236	68.7
" "	Suez.	24.60	3.86	0.003	0.019	Trace	0.098	0.236	62.8
" "	Port Said.	22.82	2.86	Trace	0.013	"	0.054	0.137	37.5
June–July	Cairo.	15.84	1.41	0.002	0.043	"	0.166	0.289	105.5
" "	Ismailia.	16.56	1.36	0.004	0.029	0.04	0.108	0.204	72.0
" "	Suez.	27.00	4.07	0.001	0.022	Trace	0.091	0.174	57.8
" "	Port Said.	20.52	2.27	0.001	0.013	"	0.053	0.106	34.4
July–August ...	Cairo.	17.16	0.64	Trace	0.016	0.03	0.089	0.145	45.2
" " ...	Ismailia.	16.08	0.67	0.003	0.021	0.07	0.079	0.145	52.2
" " ...	Suez.	22.36	3.03	0.001	0.017	Trace	0.091	0.168	52.2
" " ...	Port Said.	16.84	1.01	Trace	0.012	"	0.065	0.124	37.4

TABLE VIII. ANALYSES AT ASSIOUT, DEYROUT, AND MEDINET-EL-FAYOUM.

Date.	Place.	Total solids.	Chlorin.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.
May	Assiout.	19.96	2.45	0.012	0.039	0.09	0.148	0.267	98.1
"	Deyrout.	17.40	...	0.006	0.027	0.04	0.114	0.250	76.2
"	Fayoum.	47.32	11.73	0.002	0.037	0.01	0.110	0.226	70.0
June	Assiout.	14.60	1.32	0.073	0.059	None	0.164	0.372	143.6
"	Deyrout.	15.28	1.26	0.001	0.038	0.17	0.111	0.214	82.6
"	Fayoum.	49.28	13.00	0.002	0.025	Trace	0.080	0.135	55.9
July	Assiout.	16.36	0.68	Trace	0.010	0.02	0.089	0.145	42.4
"	Deyrout.	17.00	0.82	0.008	0.023	0.26	0.079	0.160	57.7
"	Fayoum.	27.56	4.48	0.001	0.037	0.03	0.119	0.248	85.9

Mean coefficient of purity:
Assiout................... 93.7
Deyrout 72.2
Fayoum 70.3

TABLE IX. ANALYSES AT RODAH, KASR-EL-NIL, AND AFTER KEEPING.

Place.	Total solids.	Chlorin.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.
Rodah	20.08	2.82	0.002	0.019	0.01	0.112	0.256	67.4
Kasr-el-Nil.............	19.64	2.91	0.003	0.019	Trace	0.124	0.264	70.8
Embabeh	19.72	2.82	0.004	0.018	0.01	0.129	0.275	72.1
Embabeh after 6 weeks	...	...	0.002	0.013	0.13	0.051	0.108	34.9

TABLE X. SHOWING THE EFFECT OF FILTRATION THROUGH VARIOUS MEDIA.

Desig- nation.	Ammonia. Free.	Albuminoid.	Nitric acid.	O absorbed. 15 min.	4 hrs.	Coefficient of purity.
a..........	0.010	0.021	Trace	0.127	0.200	68.4
b..........	Trace	0.016	0.03	0.089	0.145	48.4
c..........	Trace	0.009	0.13	0.057	0.080	29.0
d..........	0.014	0.005	None	0.017	0.030	14.2

In order to more readily compare the different analyses, I adopted a modification of Wigner's scale (*Analyst*, **IV.** c. f. Muter, *Analyst* **8,** 93). I do not agree with Wigner that a scale can be constructed for all waters, but I am of opinion that in a case like this, when a number of waters of the same origin have to be compared, that it is of use, though not of rigid exactitude. I wish to state distinctly that my scale is for the water of the Nile

only after double filtration through paper (and in a few other occasional cases).

In drawing up my scale and limits I took into account the origin of the impurities in the Nile, its rapid self-purification, the absence of nitrates, and other small points ; the task of giving all the reasons in detail would be too difficult and lengthy to permit their publication in a paper of this kind, and I give the scale adopted without further comment.

```
Each 0.005 parts of free ammonia ..................... = 1
 "  0.001    "    albuminoid ammonia ............... = 1
 "  0.005    "    oxygen absorbed in fifteen minutes = 1
 "  0.01     "        "         "    " four hours..... = 1
 "  0.2      "    nitric acid ......................... = 1
```

For Letheby's and Pollard's analyses

```
Each 0.005 parts of oxygen absorbed................... = 1
```

The limits I propose, are:

> Good water up to about 50.
> Moderate water from about 50 to about 100.
> Bad water over about 100.

This value I term "coefficient of purity."

In the case of waters from Wady Halfa, Assouan, and Keneh, the time of transit was longer than is desirable, and I have corrected their coefficient of purity by adding 100 per cent. to the Wady Halfa analyses, sixty per cent. to the Assouan analyses, and forty per cent. to the Keneh analyses. The figures are based on my experiments on the self-purification of the water, and give rough approximations. I have thought it more useful to employ these approximations than to reject the analyses altogether, but they can only be regarded as giving general indications.

I have had to reject the Minieh results for reasons stated below. In order to compare the results in Table V their averages are given in Table VI ; the Bahr Yousef results in Table VIII are also averaged.

The methods of the Society of Public Analysts were adopted with the following modifications :

(1) The total solids were dried at 150° C.

(2) The nitric acid was determined by the copper-zinc couple (Williams, *J. Chem. Soc.*, 1881, 100), nine-tenths of the free

ammonia being subtracted, and the remaining ammonia multiplied by 3.2 to give the quantity of nitric acid; these constants were experimentally determined for the Nile water.

(3) The suspended matter was determined by evaporating a known quantity of unfiltered water, drying at 150°, and subtracting the total solids of the filtered water.

An inspection of the tables and diagrams leads to the following conclusions:

(a) The total solids and chlorin increase regularly during the flow of the river.

(b) The coefficient of purity decreases regularly, showing a continual purification.

(c) The nitric acid is very small.

(d) The Nile in its passage through Cairo undergoes slight but distinct pollution.

(e) The Nile water on standing purifies itself (this has been otherwise confirmed).

Conclusion (a) is especially brought out by the results on the Bahr Yousef and the Lower Nile, where the current is less rapid than on the Upper Nile.

(f) Filtration purifies the water of the Nile. This will be more fully discussed under part III.

The results at Rosetta have been rejected on account of the small number of analyses, and those of Minieh because there is evidence of the samples not having been taken in accordance with directions; the Nile at Minieh is very wide (one and a half miles) and near the town the water is very shallow and has practically no current, and it is more than probable that the samples were taken at a short distance from the bank instead of in midstream. The occurrence of nitric acid at some parts and its disappearance at others caused at first some surprise, but this is probably due to the fact that the bed of the Upper Nile contains iron in the forms of ferrous and ferric silicates and magnetic oxid in considerable quantities, pointed out by Johnson Pasha and myself in a communication to the Geological Society. The absence of nitric acid at Port Said is due to the fact that the water is conveyed many miles in iron pipes; a similar disappearance of nitrates from a like cause is recorded by Harvey (*Analyst*, **14**, 34); the

suspended matter in the Nile is highly ferruginous and this plays its part, doubtless, in the disappearance of nitrates and the purification of the water. The action of iron and its compounds in purifying waters is not understood, and deserves further study.

(*g*) The Nile is at its worst just before the flood, and at its best just afterwards. There is a second small rise in the coefficient of purity about the time when the flow of the Nile is checked by the opening of the irrigation canals and basins. (This will be further discussed in Part III.)

(*h*) The total solids and chlorin vary in inverse ratio to the height of the Nile, or in other words to its bulk.

This is almost a foregone conclusion, as it is evident that a larger bulk moving at a quicker rate will not take up so large a percentage of impurity as a less quantity.

III. THE CAIRO WATER COMPANY. NOTES ON THE WATER SUPPLY AND SANITATION OF EGYPT.

The Cairo Water Company draws its supply from the Nile just below the Kasr-el-Nil Barracks; the water is pumped to the filter beds at Abbasiyah, about three and a half miles; it flows first into a tank where a proportion of the suspended matter settles, and thence to the filter beds, which are composed of sand, fine, medium, and coarse gravel, and small stones, in layers of about thirty cm. each, the total thickness being 1.75 meters, and the filtered water is received in two covered reservoirs; from these it descends by gravitation to Cairo, about two miles off.

The company has a concession from the government expiring in 1913 for the sole supply of water, both filtered and unfiltered, to Cairo ; the water is not required to be of any special purity, as long as it is *not worse than the Nile water.*

From time to time the *Bosphore Egyptien*, a Cairo journal, has complained of the quality of the water, and occasionally the government has ordered chemical investigations. The most important of these was carried out by Pappel and *Legros* in 1887, and in their report they condemned the water as bad, and recommended very radical changes in the beds of the company, including the construction of a tunnel of considerable length filled with broken bricks, the increasing of the thickness of the filtering layer to 3.75 meters, and the building of a high wall to enclose the filter

beds; they considered a settling tank not only useless, but rather injurious; no experiments were made beyond some half dozen determinations of free and albuminoid ammonia in the water and the sand of the filter beds. This report was criticised very unfavorably by Tanquerel, of Cairo, and Muntz, of Paris, and the company brought forward certain facts in their defence which led the government to drop all inquiry.

By reason of the false position in which the government was placed, it was unable to get the water company to make any improvements, and the company became skeptical concerning scientific recommendations. In 1890 an outcry against the water was again raised, and the government took the matter up and entrusted the work to my hands.

I made analyses as follows:

	Water at intake.	Water in reservoir I.	Water in reservoir II.
Total solids	14.56	14.32	14.44
Loss on ignition	1.52	1.08	1.20
Oxygen absorbed, 4 hours	0.268	0.140	0.177
Free ammonia	0.016	0.011	0.023
Albuminoid ammonia	0.039	0.009	0.011

As there was evidence of considerable purification, I reported to that effect, and refrained from offering unasked-for suggestions.

The attitude of the company became more favorable, and I believe they are quite willing to adopt any reasonable suggestions for the more efficient purification of the water. I am indebted to the kindness of the Director of the Cairo Water Company for aid in this research by the supply of sand for filtration.

TABLE XI. ANALYSES OF THE CAIRO WATER COMPANY'S WATER.

Date.	Total solids.	Suspended matter.	Chlorin.	Free Ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.	Coef. of P. ÷ Coef. of P. of Nile water.
Mar. 25, 1891	17.72	Trace	1.03	0.001	0.008	0.03	0.051	0.103	34.0	0.57
Apr. 23, 1891	24.70	None	2.21	0.004	0.007	0.01	0.048	0.119	29.3	0.43
May 26, 1891	20.76	"	3.14	0.001	0.009	0.08	0.064	0.189	41.3	0.58
June 29, 1891	18.80	"	1.43	0.001	0.024	0.01	0.069	0.149	52.9	0.50
July 28, 1891	18.60	Trace	0.91	Trace	0.009	0.13	0.057	0.080	29.0	0.60
Aug. 28, 1891	17.24	"	1.02	0.001	0.007	0.05	0.053	0.082	26.2	0.61
Sept. 31, 1891	14.12	"	0.79	0.001	0.005	0.08	0.045	0.092	23.8	0.67

In Table XI are given the results of the analyses of the water of

the company made contemporaneously with those of the Nile at Cairo.

It is seen that the total solids and the chlorin remain almost the same as the quantities found in the Nile, the slight increase in the chlorin being due to the presence of small quantities of salt in the sand; the coefficient of purity is, however, in all cases diminished about fifty per cent. The filters of the Cairo Water Company then do their work properly, and result in a purification of the Nile water. Judged by my scale, the water may be, except perhaps in June, considered good.

As the word "good" in water analysis is used somewhat loosely, and does not mean perfect, I instituted experiments in order to find out a better means of purifying the Nile water; it is not necessary to detail the experiments, and I only give (in Table X) the figures of one of them. Four samples of the same water were examined.

(*a*) After precipitation of the suspended matter by a very small quantity of ferric chlorid.

(*b*) After filtration as usual through double filters.

(*c*) After filtration through a layer of sand the same thickness as used by the Cairo Water Company.

(*d*) After filtration through a layer of fine sand 0.75 meter thick, a layer of "polarite" 0.20 meter thick, and a layer of coarse sand 0.75 meter thick.

From the results it is seen that filtration, even through paper (and its own suspended matter), improves the Nile water, doubtless assisted by the large surface exposed to the air; filtration through sand improves it still more, and after filtration through "polarite" very little fault can be found with the water. The "polarite" in this case has exercised a reducing influence on the nitrates; this is not always the case, and seems to take place when the "polarite" is fresh. In all my experiments the "polarite" purified the water to the extent of about eighty per cent., judged by my scale; as to the exactness of this figure I cannot vouch, but it is certain that no other filtering material has given such satisfactory results in my hands. I therefore can strongly recommend the use of "polarite" to the Cairo Water Company. I may mention that this material was handed to me with the simple

description of "material for purifying water" and it was only after some difficulty that I established its identity. The monthly variations of the water of the company follow those of the Nile; the quality of the water in the river is dependent on the following :

(a) The (presumable) purity in the water of the Nyanzas and of the rainfall collected by the great watersheds of the White, the Blue, and the Black, Nile; (b) the taking up of impurities in the marshy districts of Central Africa; (c) the taking up of impurities during its flow, and the pollution of the river established at Cairo and more than probable at other points; (d) the self-purification of the river, in which the minerals in its bed and the suspended matter, probably aid the oxygen of the air. The quality of the Company's water is also dependent on (e) the filtering materials used.

The water at Port Said (q. v.) is analogous to the Cairo Water Company's water, as it is filtered at Ismailia before traversing the iron pipes which convey it to Port Said. The absence of nitrates at Port Said has already been explained.

<div align="center">[TO BE CONTINUED.]</div>

RAPID DETERMINATION OF PHOSPHORUS IN COAL AND COKE.

BY FRANK L. CROBAUGH, B.S.

Place five gms. of very finely pulverized material in a large platinum crucible, incline over a four tube Bunsen burner. So adjust the flame that the crucible is about one-half surrounded by it. By occasional thorough stirring the carbon will be nearly completely burned within two hours. Allow the crucible to cool, then add about five gms. of sodium carbonate and about one-half gm. of potassium nitrate. Mix this with the ash by aid of a platinum wire. Place the covered crucible over the four-way burner until a liquid fusion has continued for five minutes. The potassium nitrate will have destroyed the last traces of carbon, as well as having rendered the fusion more fluid and easily soluble. Allow the crucible to cool and place it in a beaker containing about 150 cc. of nitric acid, 1.135 sp. gr., in which at a gentle heat it will be most readily taken up. Filter at the pump

through a tight filter from the flotant matter, into a shaking flask, and proceed as in this Journal, **6,** No. 9, September, 1892. The amount of labor required is small, and the results accurate:

THE MANUFACTURE OF NITROGLYCEROL.

BY P. GERALD SANFORD, F. I. C., F. C. S.

One of the most powerful of modern explosive agents is nitroglycerol. It is the explosive material contained in dynamite, and forms the greater part of the various forms of blasting gelatins, such as gelatin dynamite and gelignite, both of which substances consist of a mixture of gun cotton dissolved in nitroglycerol, with various proportions of wood pulp and saltpeter, the latter substances acting as absorbing materials for the almost liquid, or rather viscid gelatin. The gelatin itself is made by dissolving the lower nitrates of cellulose, known as collodion cotton, or technically as dinitrocellulose, in nitroglycerol. Nitroglycerol, or glycerol trinitrate, was discovered by Sobrero in the year 1847. In a letter written to M. Pelouse he says that ''when glycerol is poured into a mixture of sulphuric acid of a specific gravity of 1.84 and of nitric acid of a gravity of 1.5, which has been cooled by a freezing mixture, that an oily liquid is formed.'' This liquid is nitroglycerol, which for some time found no important use in the arts, until the year 1863, when Nobel first started a factory in Stockholm for its manufacture upon a large scale; but on account of some serious accidents taking place, its use did not become general. It was not until Nobel conceived the idea (in 1866) of absorbing the liquid in some absorbent earth, and thus forming the material that is now known as dynamite, that the use of nitroglycerol as an explosive became general. Among those who improved the manufacture of nitroglycerol was Mowbray, who, by using pure glycerol and nitric acid free from nitrous acid, made very great advances in the manufacture. Mowbray was probably the first to use compressed air for the purpose of keeping the liquids well agitated during the process of nitration, which he conducted in earthenware pots, each containing a charge of seventeen pounds of the mixed acids and two pounds of glycerol. A few years later (1872) MM. Vouges

and Boutnny [1] proposed to prepare nitroglycerol by mixing the sulfuric acid with the glycerol, thus forming a sulfoglyceric acid, which was afterwards mixed with a mixture of nitric and sulfuric acids; they claim for this method of procedure that the final temperature is much lower.   The two mixtures are mixed in the proportions: Glycerol, 100; nitric acid, 280; and sulfuric acid, 600. They state that the rise of temperature upon mixing is limited from 10° to 15° C.; but this method requires a period of twenty-four hours to complete the nitration, which, considering the danger of keeping the nitroglycerol in contact with the mixed acids for so long, probably more than compensates for the somewhat doubtful advantage of being able to perform the nitration at such a low temperature.   The Boutnny process was for some time in operation at Pembrey Burrows, in Wales, but after a serious explosion the process was abandoned.   Nitroglycerol is now generally made by adding the glycerol to a mixture of sulfuric and nitric acids; the sulfuric acid however takes no part in the reaction, but is absolutely necessary, to combine with the water that is formed by the decomposition, and thus to keep up the strength of the nitric acid, otherwise lower nitrates of glycerol would be formed that are soluble in water, and which would be lost in the subsequent process of washing to which the nitro compound is subjected, in order to remove the excess of acids, the retention of which in the nitroglycerol is very dangerous. Nitroglycerol, which was formerly considered to be a nitrosubstitution compound of glycerol, was thought to be formed thus:

$$C_3H_5O_3 + 3HNO_3 = C_3H_5(NO_2)_3O_3 + 3H_2O$$
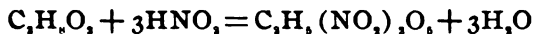
but more recent researches rather point to its being regarded as a nitric ether of glycerol, and to its being formed thus:

$$\underset{92}{C_3H_5O_3} + 3HNO_3 = \underset{227}{C_3H_5(NO_3)_3} + 3H_2O$$
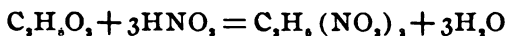
In the manufacture upon the large scale, a mixture of three parts by weight nitric acid, and five parts of sulfuric acid are used.   From the above equation it will be seen that every one pound of glycerol should give 2.47 pounds of nitroglycerol ($\frac{227+1}{92} = 2.47$), but in practice, the yield is only about two

[1] *Comptes Rendus*, 75; and *Desortiaux Traité sur la Poudre*, 684-686.

pounds, the loss being accounted for by the unavoidable forma-
tion of some of the lower nitrates of glycerol, which dissolve in
water and are thus washed away, and partly, perhaps, to the pres-
ence of a little moisture in the glycerol, but chiefly to the former.

PROPERTIES OF NITROGLYCEROL.

Nitroglycerol is a heavy oily liquid of a sp. gr. of 1.6 at 15° C.
and when quite pure is colorless; the commercial product
is pale straw yellow, but varies much according to the purity of
the materials used in its manufacture. When pure it may be kept
any length of time without decomposition. Berthelot kept a
sample for ten years, and Mr. G. McRoberts of the Ardeer factory
for nine years without their showing signs of decomposition, but
if it should contain the smallest trace of free acid, decomposition
is certain to be started before long. This will generally show
itself by the formation of little green spots in the gelatin compounds,
or a green ring upon the surface of the liquid nitroglycerol.
Sunlight will often cause it to explode; in fact, a bucket con-
taining some water that had been used to wash nitroglycerol, and
had been left standing in the sun, has in our experience been
known to explode with considerable force. Nitroglycerol freezes
at +8° to —11° C., but different commercial samples behave
very differently in this respect, and minute impurities prevent
or delay crystallization. Solid nitroglycerol melts at from 10°
to 11° C., but requires to be exposed to this temperature for some
time before melting. The specific gravity of the solid form is 1.735
at +10° C.; it contracts one-twelfth of its volume in solidifying.
Beckerheim[1] gives the specific heat as 0.4248 between the tem-
peratures of 9.5 and 9.8° C. Nitroglycerol has a sweet taste, and
causes great depression and vertigo; it is soluble in ether, chloro-
form, benzene, glacial acetic acid, and nitrobenzene, soluble in
1.75 parts of methylated spirit, very nearly insoluble in water,
and practically insoluble in CS_2. Its percentage composition is
as follows:

	Found.	Theory for $C_3H_5(NO_3)_3$.
Carbon	15.62	15.86 per cent.
Hydrogen	2.40	2.20 "
Nitrogen	17.90	18.50 "
Oxygen	....	63.44 "

[1] Jsb. chem. Techn., 22, 481-7, 1876.

The above analysis is by Beckerheim; Sauer and Adou give the nitrogen as 18.35 to 10.54 per cent. by Dumas' method, but I have never found any difficulty in obtaining percentages as high as 18.46 by the use of Lunge's nitrometer. The decomposition products by explosion are shown by the following equation :

$$2C_3H_5(NO_3)_3 = 6CO_2 + 5H_2O + 6N + O$$

that is, it contains an excess of 3.52 per cent. of oxygen above that required for complete combustion.   100 gms. would be converted into

       Carbonic acid (CO_2)················ 58.15 per cent.
       Water······························· 19.83   "
       Oxygen ···························· 3.52   "
       Nitrogen··························· 18.50   "

The volume at 0°C. and 760 mm. of the gases produced by detonation, calculated from the above, is 714 liters per kilo, the water being taken as gaseous.   In a recent communication, P. F. Charon (see *Engineering and Mining Jour.*, 1892) says, that in practice nitroglycerol vapor, carbon monoxid, and nitrous oxid are also produced as the result of detonation, but he attributes their formation to the use of a too feeble detonator. Professor C. E. Munroe gives the firing point of nitroglycerol as 203°–205° C.   He used the apparatus devised by Horsley.

THE GENERAL ARRANGEMENT OF THE DANGER AREA.

That portion of the works that is devoted to the actual manufacture of explosive material is generally designated by the term "danger area" and the buildings erected upon it, are spoken of as "danger buildings."   The best material of which to construct these buildings is of wood, as in the event of an explosion they will offer less resistance, and will cause much less danger than brick or stone buildings; when an explosion of nitroglycerol or dynamite occurs in one of these buildings, the sides are generally blown out, and the roof is raised for some considerable height, and finally descends upon the blown out sides; if on the other hand the same explosion occurs in a strong brick or stone building, the walls of which would offer a much larger resistance, large pieces of brickwork will probably be thrown for a considerable distance, and cause serious damage

to surrounding buildings. It is also a very good plan to sur-
round all danger buildings with mounds of sand, or earth, which
should be covered with turf, and of such a height as to be above
the roof of the buildings that they are intended to protect. These
mounds are of great value in confining the force of the explosion,
and the sides of the buildings being thrown against them are
prevented from traveling any distance. In gunpowder works
it is not unusual to surround the danger buildings with trees, or
dense underwood, instead of mounds. In Great Britain, it is
necessary that all danger buildings should be a specified dis-
tance apart; a license also must be obtained for each building.
The selection of a site for the danger area requires some atten-
tion; the purpose for which it is required, that is the kind of
explosive that is to be manufactured, must be taken into con-
sideration. A perfectly level piece of ground might probably
be quite suitable for the manufacture of gun cotton, gun pow-
der, and such materials, but would be more or less unsuitable
for the manufacture of nitroglycerol, where a number of build-
ings are required to be upon different levels, in order to allow of
the flow of the liquid nitroglycerol from one building to another
through a system of conduits; these conduits (which are gener-
ally made of wood and lined with lead, the space between the
woodwork and the lead lining, which is generally some four or
five inches, being filled with cinders) connect the various build-
ings, and should slope gently from one to the other; it is also
desirable that as far as possible they should be protected by
earthwork banks, in the same way as the danger buildings them-
selves; they should also be provided with covers, which should
be whitewashed in hot weather. A great deal of attention
should be given to these conduits and they should be very fre-
quently inspected. Whenever it is found that a portion of the
lead lining requires repairing, before cutting away the lead it
should be very carefully washed for several feet on either side of
the portion that it is intended to remove, with a solution of caustic
soda or potash dissolved in methylated spirit and water, and
afterwards with water alone; this decomposes the nitroglycerol,
forming glycerol and potassium nitrate. It will be found that
the mixed acids attack the lead rather quickly, forming sulfate

and nitrate of lead, but chiefly the former; it is on this account that it has been proposed to use pipes made of gutta percha, but the great drawback to their use is that in the case of anything occurring inside the pipes, such as the freezing of the nitroglycerol in the winter, it is far more difficult to find it out, and the condition of the inside cannot be seen, whereas in the case of wooden conduits it is an easy matter to lift the lids along the whole length of the conduit. The buildings which require to be connected by the conduits, are, of course, those concerned with the manufacture of nitroglycerol; these buildings are: (1) the nitrating house; (2) the separating house; (3) the filter house; (4) the secondary separator; (5) the deposit of washings; (6) the settling or precipitation house; and each of these buildings must be on a level lower than the preceding one, in order that the nitroglycerol or acids may flow easily from one building to the next. These buildings are, as far as possible, best placed together, and away from the other danger buildings, such as the cartridge huts and dynamite mixing houses; but this is not essential. They should all be protected by a lightning conductor, or covered with barb wire, as suggested by Professor Oliver J. Lodge, and everything possible should be done to keep them as cool as possible in the summer; with this object, they should be made double, and the intervening space filled with cinders; the roof also should be kept whitewashed, and the windows painted over thinly with white paint; a thermometer should be suspended in every house. It is very essential that the floors of all these buildings should be washed every day before the workpeople leave. In case any nitroglycerol is spilt upon the floors, after sponging it up, as far as possible, the floor should be washed with an alcoholic solution of soda to decompose the nitroglycerol, which it does according to the equation:

$$C_3H_5(NO_3)_3 + 3KOH = C_3H_8O_3 + 3KNO_3$$
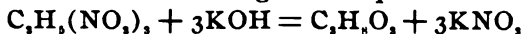
[TO BE CONTINUED.]

FUEL VALUE OF GASES.

BY H. L. PAYNE.

Data for calculating the theoretical heating power of the various combustible gases are quite widely scattered through our chemical literature and as a consequence chemists and gas engineers are very apt to use different sets of figures as a basis of calculation. Quibbling disagreements are the only result of such practice, and when we find that experts in gas matters disagree even after starting from the same figures, it becomes at times very annoying. Such variations can only arise from a difference in the methods of solving the problems and can certainly be avoided. Oftentimes a difference apparently exists, arising from a loose manner of stating just what the numerical results signify. With the hope of clearing up some of these discrepancies, I give in detail the data which I have adopted and also a full explanation of the methods of calculation.

The heat of chemical combination has been determined by many experimenters and from an extended review of the results as published in the original articles, the data furnished by Prof. Julius Thomsen of Copenhagen seem most worthy of acceptance. His results are corroborated by subsequent workers, and I have taken from his *Thermochemische Untersuchungen* the following numerical data as a basis of calculations, neglecting decimals beyond the limits of experimental error.

Substance.				Calories.
H	completely oxidized, evolves			34200
C	"	"	"	8083
CO	"	"	"	2427
CH_4	"	"	"	13245
C_2H_6	"	"	"	12350
C_3H_8	"	"	"	12028
C_4H_{10}	"	"	"	11850
C_5H_{12}	"	"	"	11770
C_6H_{14}	"	"	"	11620
C_2H_4	"	"	"	11910
C_3H_6	"	"	"	11900
C_2H_2	"	"	"	11925
C_6H_6	"	"	"	10250

Since the results of gas analyses are stated volumetrically the

calculation of a number of analyses is greatly facilitated if we convert these calories per gram into heat units per volume, and custom requires that results shall be stated in British Thermal Units per cubic foot of gas. Hence the following deductions.

Calories per gm. multiplied by $\frac{9}{5}$—the ratio of the Fahrenheit thermometer degree to the Centigrade—will give British Thermal Units per lb.

$$C \times \tfrac{9}{5} = \text{B. T. U. per pound.}$$

Dividing this result by the number of cubic feet of each gas per pound will give B. T. U. per cubic foot. To calculate the cubic feet per pound of a gas we shall have use for the following fundamental relations:

1 lb. = 453.59 gms. 1 meter = 39.37 inches. 1728 (cu. in. to 1 cu. ft.) divided by $(3.937)^3 = 28.317$; therefore, 1 cu. ft. = 28.317 liters.

Using these figures our formula for calculation is: B. T. U. per cubic foot $= C \times \tfrac{9}{5} \times \tfrac{28.317}{453.59} \times$ the liter weight in grams of the gas in question.

The following table contains the liter weights as determined by actual weighing of some of the gases:

Gas.	Grams per liter.	Gas.	Grams per liter.
H	0.08988	CO	1.251
O	1.430	CO_2	1.966
N	1.257	CH_4	0.7155
Air	1.293	C_2H_4	1.252

For the other hydrocarbons and gases not given above, we may substitute in the formula in place of liter weight the expression $\left(\tfrac{\text{molecular weight}}{2} \times \tfrac{0.08988}{1.007}\right)$. This formula then may be reduced to the following form, B. T. U. per cubic foot $= C \times \tfrac{\text{mol. weight}}{2} \times 0.01003$, which is comparatively simple and can be used in all cases without very serious error. In this formula as elsewhere the atomic weights to be used are those given by F. W. Clarke, dated December 6, 1890. (See this Journal for February, 1891.)

Element.	At. Wt.	Element.	At. Wt.
H	1.007	N	14.03
O	16.00	C	12.00

Applying these formulas to the different combustible gases I

have deduced the following figures which it is proposed to use in all published work:

Gas.	B. T. U. per cu. ft.	Gas.	B. T. U. per cu. ft.
(1) H	345.4	C_5H_{12}	4255.
(2) CO	341.2	C_6H_{14}	5017.
(3) CH_4	1065.		
(4) Illuminants	2000.	C_2H_4	1674.
C_2H_6	1861.	C_3H_6	2509.
C_3H_8	2657.		
C_4H_{10}	3441.	C_6H_6	4012.

To calculate the heat units of a gas from its analysis, multiply the per cent. of each constituent by its number as given in the above table, and the sum of the products will represent the British Thermal Units evolved by the combustion of one cubic foot of the gas.

Ordinary gas analysis includes only the first four of these combustibles, and for those hydrocarbons which are determined by absorption in bromin or fuming sulfuric acid, generally designated as "illuminants," I have given the heating value 2000. This has proven to be a very trustworthy value where the hydrocarbons are derived chiefly from the decomposition of mineral oil, but if produced by the distillation of coal this value is too low, owing to a larger percentage of benzene vapors contained.

The experimental conditions necessary to give these theoretical results are that the gas is measured at 32° F. and 760 B., and is burned with exactly the proper quantity of oxygen, and that the products of combustion are reduced to the initial temperature, the water being all in a liquid state. It is superfluous to say that this can not actually be done; but as the whole matter is a theoretical discussion, I have decided to adhere to the scientific standard, and to state results in accordance with its definitions. But in order to obtain figures which shall more nearly agree with practice, many persons have preferred to make their calculations under certain assumed conditions. This plan is not without merit, since by it a somewhat better idea of the true relative values of fuel constituents is obtained, similar conditions affecting different gases unequally. To illustrate this method I add the following examples.

The temperature for standard gas measurement in this coun-

try is 60° F. and this point is usually assumed as the initial temperature. As a final temperature in this case let us assume the temperature of steam at 100 lbs. absolute pressure per square inch (328° F.), a point somewhat lower than the average chimney-flue heat. Under these conditions combustion taking place in air, not pure oxygen, we must add the heat brought in by the gas and air at 60° and subtract the heat carried away by the products of combustion at 328°. And since the volume of the gas is greater at 60° than at 32°, we correct for this by multiplying the result by $\frac{492}{492+28}$ or $\frac{492}{520}$.

The composition of air is:

	By volume.	By weight.
Oxygen	20.92 per cent.	23.134 per cent.
Nitrogen	79.08 "	76.866 "

Hence 4.78 volumes air contain one volume O, or one volume O is accompanied by 3.78 volumes N.

The specific heats of the several gases are as follows:

Gas.	Specific heat.	Gas.	Specific heat.
H	3.4	CO	0.25
O	0.22	CO_2	0.22
N	0.24	CH_4	0.60
Air	0.24	Illuminants	about 0.40

It will be more convenient in these computations to make use of the so-called "volumetric" specific heats, i. e., the heat necessary to raise the temperature of one cubic foot of gas from 32° to 33° F.[1]

Gas.	Vol. specific heat.	Gas.	Vol. specific heat.
H	0.019	Co	0.019
O	0.019	CO_2	0.027
N	0.019	CH_4	0.027
Air	0.019	Illuminants	about 0.04

Our calculations then proceed as follows:

$$2 H + O + 3.78 N = H_2O + 3.78 N; \text{ or,}$$
1 cu. ft. H + 2.39 cu. ft. air = 1 cu. ft. steam + 1.89 cu. ft. N.
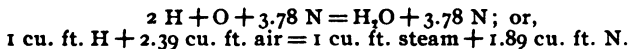
The heat gained or brought in is as follows:

$$H = 1 \times 0.019 \times 0.28 = 0.53 \text{ B. T. U.}$$
$$Air = 2.39 \times 0.019 \times 0.28 = 1.27 \text{ "}$$

Total gain 1.8 "

[1] For general purposes it is sufficiently accurate to take the vol. specific heat of gaseous mixtures as 0.02.

Heat lost or carried away by products of combustion. Water at 32° converted into steam at 328° absorbs 1182 B. T. U. per pound and one cubic foot H produces when burnt 0.0502 pounds water.

$$\text{Steam} = 0.0502 \times 1182 = 59.4 \text{ B. T. U.}$$
$$N = 1.89 \times 0.019 \times 296 = 10.6 \quad \text{``}$$

$$\text{Total loss } 70.0 \quad \text{``}$$
$$\text{Subtract gain } 1.8 \quad \text{``}$$

$$\text{Net loss } 68.2 \quad \text{``}$$

345.4 B. T. U., less 68.2 B. T. U., leaves 277.2 B. T. U. This corrected for volume gives 262.3 B. T. U., a loss of 24 per cent.

In the case of CO no water is produced by combustion and the former value is consequently much less affected.

One cubic foot CO + 2.39 cubic feet air = 1 cubic foot CO_2 + 1.89 cubic foot N.

Heat gained or brought in by CO and air the same as H and air in the previous case, 1.8 B. T. U.

Heat lost:

$$CO_2 = 1 \times 0.027 \times 296 = \quad 8.0 \text{ B. T. U.}$$
$$N = \text{as above} \quad 10.6 \quad \text{``}$$

$$\text{Total loss } 18.6 \quad \text{``}$$
$$\text{Subtract gain } 1.8 \quad \text{``}$$

$$\text{Leaves a net loss } 16.8 \quad \text{``}$$

341.2 B. T. U., less 16.8 B. T. U., leaves 324.4 B. T. U. This corrected for volume gives 306.9 B. T. U., a loss of only 10 per cent.

For marsh gas:

1 cu. ft. CH_4 + 4 (2.39 cu. ft. air) = 1 cu. ft. CO_2 + 2 cu. ft. steam + 4 (1.89 cu. ft. N).

Heat gained:

$$CH_4 = 1 \times 0.027 \times 28 = 0.8 \text{ B. T. U.}$$
$$\text{Air} = 4 \times 1.27 \text{ B. T. U.} = 5.1 \quad \text{``}$$

$$\text{Total gain } 5.9 \quad \text{``}$$

Heat lost:

$$CO_2 = 1 \times 0.027 \times 296 = \quad 8.0 \text{ B. T. U.}$$
$$\text{Steam} = 2 \times 59.4 \text{ B. T. U.} = 118.8 \quad \text{``}$$
$$N = 4 \times 10.6 \text{ B. T. U.} = \quad 42.4 \quad \text{``}$$

$$\text{Total loss } 169.2 \quad \text{``}$$
$$\text{Subtract gain } 5.9 \quad \text{``}$$

$$\text{Leaves a net loss } 163.3 \quad \text{``}$$

1065 B. T. U., less 163.3 B. T. U., leaves 901.7 B. T. U. This corrected for volume gives 853.0 B. T. U., a loss of 20 per cent.

For "illuminants" fifteen per cent. is taken as a fair loss and our values stand thus:

Gas.	32° initial, 32° final.	60° initial, 328° final.	Lost in per cent.
H...............	345.4	263.2	24
CO..............	341.2	306.9	10
CH₄..........	1065.0	853.0	20
Illuminants...	2000.0	1700.0	15

Natural gas has been taken as a standard for heating gases and is called 1000. At ninety-four per cent. CH_4 which is not far from the average, it will show by our calculation 1000 B. T. U. per cubic foot and hence the numerical result obtained by this method for any fuel gas will indicate also its standing in that scale.

A SIMPLE METHOD FOR THE SEPARATION OF IRON AND ALUMINA.[1]

By H. Bornträger.

As is well known iron and alumina are precipitated together in an analysis by means of ammonia as hydroxids, especially in fertilizer analysis. They are somewhat difficult to separate by the methods heretofore used. I describe below a tolerably exact and simple method. The hydroxids are first precipitated together, heated and weighed as oxids; they are then dissolved in hydrochloric acid made almost neutral with potassium hydroxid—not sodium hydroxid, since sodium oleate is insoluble—and both oxids precipitated with neutral potash soap, such as has been placed on the market by the firms A. Keysser, Hanover, and A. Gude, Leipzig. The precipitation must be made hot, and an excess of soap must in all cases be avoided, since otherwise the oleates redissolve. The solution is filtered through a filter wetted with hot water; the precipitate, which, when iron is present, has a reddish-brown color, washed with hot water until the potassium chlorid is removed and the precipitate dried somewhat over calcium chlorid until most of the water disappears, and the gelatinous mass treated with hot petroleum until the filtrate is colorless and all the iron oleate has gone into solution. The filter is then burned and the

[1] *Ztschr. anal. Chem.*, 32, 187.

remaining snow-white alumina weighed.   The petroleum solution may also be evaporated and the iron determined by ignition. Ferrous as well as ferric oxid may be separated from alumina in this way, since both oleates dissolve easily in petroleum.   As only minimum amounts of alumina dissolve, the results are very exact.

PATENTS OF INTEREST TO CHEMISTS.
EDITED BY A. H. WELLES.

John W. Marshall is the patentee of an ore stamping mill (493,384) and of an ore stamp (493,385).   Wm. Birkin subjects ores to the action of potassium cyanid, potassium ferricyanid, and hydrogen peroxid to extract the precious metals (494,054). Charles J. Fauvel has a new furnace for the treatment of refractory ores (493,076).   A process for roasting sulfur bearing ores and obtaining sulfur in the solid form, Charles W. Stickney, inventor, consists in roasting one portion by means of steam and mechanical agitation, generating hydrogen sulfid, and roasting another portion by means of air, generating sulfur dioxid, and mingling these gases in contact with a solution of a sulfate of a heavy metal (493,193).   Jabez Turton proposes to separate metals from ores by treating the ore or mineral to the action of a nitrate of an alkali metal, sodium chlorid, and sulfuric acid, separating the earthy matters and precipitating the metals (494,044).   W. T. Gibbs and S. P. Franchot (493,023) patent their process for obtaining chlorates of the alkalis or the alkaline earths by electrolysis, while O. Lugo (493,277) deposits metals from a liquid paste composed of a mixture of the insoluble salts of the metals with water by passing the electric current.

Karl Sundstrom (492,929) has an improvement in the manufacture of soda.   Bicarbonate mud is first purified by dissolving out the ammonia compounds with a suitable solvent, then passing water in a finely divided spray to remove the sodium chlorid. To convert insoluble hydrated phosphates of alumina into soluble forms, Stephen L. Goodale heats the hydrates in suitable receptacles until the water of combination is expelled and then allows the phosphates to cool spontaneously (493,889).

For the lixiviation of gold and silver ores, Samuel R. Whitall first mixes them with either caustic soda or potash, then treats with a solution of potassium cyanid and sodium hyposulfite and precipitates the precious metals by electrolysis (495,715). Fred. Webb has an apparatus for extracting precious metals from their ores (495,385), and John F. Wiswell treats ores as follows : Mercury is submerged in a solution of common salt which is electrolysed. The calomel formed is dissolved in aqua regia, forming mercuric chlorid, while the indecomposed salt solution is further electrolysed, forming sodium hypochlorite. The ores are then treated simultaneously with both solution of the hypochlorite and mercuric chlorid, and the dissolved metals are precipitated by adding bright iron fragments (495,212). George Wegner and Paul Gührs prepare articles to be electroplated with aluminum by first steeping in a bath of ''acetic verdigris dissolved in vinegar,'' oxid of iron, sulfur and ammonium chlorid, brushing after removal from bath with a soft brass wire brush and rinsing with water (496,176). F. J. Clamer's method for coating metal articles, is first to clean by making them anodes in an electrolytic cell, then washing in a bath of dilute hydrochloric acid, immersing next in a bath of molten lead and phosphorus, and finally subjecting to pressure (494,667 and 668).

James B. Montgomery has a new form of ore concentrator (495,003). Orrin B. Peck adds one more to his list of patents on a centrifugal ore separator (495,681), and M. W. Iles covers his process of an apparatus for the extraction of matte from slag by numbers 494,570 and 494,571. A. L. Engelbach and S. E. Bretherton have an apparatus for reducing and smelting sulfid ores (496,250). Charles M. Allen takes out three related patents ; 496,032 treats of his process of smelting ores and refining metals which is conducted in a converter (496,033), which has a patent tuyere (496,034). The ores are fed into this converter and the blast is passed through the molten metal for a time, then checked by plugging the tuyeres to permit slag, matte, and metal to separate in the converter at different heights, and enough molten metal is retained each time to ignite the next charge.

Johannes Pfleger has an electrolytic process for zinc (495,637). It is described as consisting in adding a basic zinc salt solution

to a zinc-containing anode, to which basic zinc solution a con-
ducting neutral salt has been added. George T. Lewis treats
roasted zinc sulfid ores by adding sodium nitrate or its equivalent
to unite with the sulfur left, roasting to form soluble sulfate,
leaching out, oxidizing the zinc in the ores thus freed from sulfur
and collecting the zinc oxid fumes (495,593). G. M. Gouyard
concentrates zinc bearing sulfids by roasting the ores, and at the
final stage employing a low heat, adding a small per cent. of finely
pulverized coal in a reducing atmosphere, which renders the iron
present magnetic and precipitates the lead on the iron, and then
separating the iron with a magnetic separator (495,550). Zinc
oxid is prepared by the method of Carl V. Petraeus from sulfid
ores by subliming the zinc, reducing the temperature of the gases
and zinc oxid driven off below a bright red heat, catching the
zinc oxid fumes, and finally heating at a red heat to whiten and
free from sulfur compounds (496,205).

John A. Just decomposes the manganese dioxid and chlorid
left after the evolution of chlorin, with nitric acid, removes the
manganous nitrate to a neutralizing well, adds manganese pro-
toxid, hydrate, or carbonate, transfers to a settling tank, then
to a concentrator worked by waste heat, next to calcining fur-
naces to decompose, condensing evolved gases and recovering
the nitric acid (495,462).

Robert Reiman chemically dissolves natural bone or bone
meal into its constituents, precipitating these elements, filters
and washes and afterwards mixes with albumen, aluminum sul-
fate, and cellulose in solution, dries partly, then subjects to a
high temperature and powerful pressure simultaneously, thus
manufacturing artificial bone (494,891). To prepare basic bis-
muth gallate, which is described as a yellow powder, odorless, in-
soluble in water, dilute acids, alcohol and ether, but soluble in a
large excess of mineral acids and containing 55–56 per cent. Bi_2O_3.
Arthur Liebricht uses the method following : Neutral bismuth
nitrate is dissolved in dilute nitric acid, a solution of gallic acid,
alcohol, and water is added, and to this mixture caustic alkali
or alkali carbonate until just slightly acid, when the salt is pre-
cipitated either with sodium acetate or by diluting with water
(495,497). Emil Jacobsen forms sulfur compounds of hydrocar-

bons, according to his patent, 495,343, and Adolf Spiegel describes his method of obtaining sulfo-compounds in 495,124. Hydrocarbons are treated first with caustic soda, then with sulfuric acid, washed with water and brine successively, and the washed product is neutralized with alkali and the sulfo products separated by some suitable solvent. Leonard Paget has five patents, the first and second, 494,790 and 495,263, on pyroxylin solvents, the other three on pyroxylin compounds—494,791, 494,792, 494,793. Dieudonnés Rigole extracts gutta percha from the leaves and twigs of the gutta percha tree, according to 495, 757.

[The specification and drawing of any U. S. Patent in print may be obtained from the publisher of this Journal. Applications must be accompanied in all cases by twenty-five cents for each patent specification wantéd. BE CAREFUL TO WRITE THE NUMBER LEGIBLY.]

NOTES.

Post Mortem Imbibition of Arsenic.—

STATE AGRICULTURAL COLLEGE.

Fort Collins, Col., April 7, 1893.

Prof. Edward Hart;

Dear Sir:

A few years ago I was a witness in a murder trial. It was claimed by the defense that if arsenical compounds were used to embalm the body, that arsenic would be found in the bones. The solution used to embalm the body in this case was about a ten per cent. solution of sulfate of zinc. In the bottom of the carboy there was a very small quantity of an insoluble compound of arsenic and lime (in the whole carboy full not one-tenth part of what was found in the bones). Arsenic was found in the ribs, femur, tibia, etc., of both sides; also in the muscles adjoining these bones. The subject of *post mortem imbibition* of arsenic in the muscles, is spoken of in *Wormley on Poisons*, second edition, pp. 313 to 315. It has been clearly shown that the longer the delay after death the less the diffusion of the poison, and that when decomposition has set in diffusion will be arrested. I have not been able to find any statement about this diffusion of arsenic in the bones. To settle the question in my mind I tried the following experiment: I killed a young dog that would weigh about ten kilos, with chloroform. The viscera was removed in order to bring it in close contact with the flesh and ribs. Immediately after the viscera was removed I dissolved ten grams of As_2O_3

in caustic potash and water, in all abont 600 cc., and this solution was poured over the interior of the body walls. The body was buried February 13, 1892, in a box about one meter below the surface of the soil. The dog remained undisturbed till February, 6, 1893, when he was removed. The flesh in the region of the ribs was apparently in a state of perfect preservation. The bones were scraped and washed with a brush and hot water, dried, pulverized and treated as described in Fresenius *Quantitative Analysis*, pp. 781–786. The humerus, radius, ulna, were mixed together and tested for arsenic by the above described method, and no trace of arsenic could be found. The ribs when similarly treated showed the presence of arsenic in small quantities. There seems to my mind but one conclusion; that when arsenic is found in the bones remote from the viscera it is the result of ante and not post mortem imbibition.

D. O'Brine.

Fees for Assays and Analyses in South Australia.—The following scale of charges is taken from the Annual Report of the South Australian School of Mines and Technological Museum for 1892 :

SCALE OF CHARGES.

	£	s.	d.
Bullion Assays—Single Assay of Gold or Silver	o	5	o
" " Two or more Assays of Gold or Silver, each	o	4	o
Assay of Gold Quartz, Blanketings, Pyrites, Tailings, etc., for Gold or Silver	o	10	6
Examination of Mineral for any Valuable Metal	o	10	6
Complete Quantitative Analysis of Mineral or other Substance, according to the Number of Substances to be determined, from	3	3	o
Assay of Lead, Copper, Tin, Silver, Iron, Manganese, or other Ore, for the one Metal	o	10	6
Assay of Lead, Copper, Tin, Silver, Iron, Manganese, for two or three Metals, as Lead, Silver, Gold; Copper, Silver, Gold	1	1	o
Determination of Mineral, Rock, or Fossil, according to Mineralogical or Geological order—Single Specimen	o	5	o
A Collection, according to arrangement.			
Analysis of Iron, for any one Substance, as Carbon, Silicon, Sulfur, Phosphorus, &c.	o	15	o

Prospectors and others interested in mines or minerals may make special arrangements to perform determinative experiments in the laboratory, under the supervision of the school officers, at 1 s. per hour.

N. B.—Samples submitted for assay or analysis must be accompanied by check, postal order, or stamps. covering charges, and addressed to the Registrar, School of Mines, North-terrace.

=======THE=======

Journal of Analytical & Applied Chemistry.

THE RIVER NILE.

BY H. DROOP RICHMOND, LATE SECOND CHEMIST TO THE EGYPTIAN GOVERNMENT.

(Continued from page 223.)

Y recommendation to the Cairo Water Company may profitably be extended to the other towns of Egypt; the Alexandria Water Company adopts a modification of Anderson's process, the short canal conveying the water from the Mahmoudieh Canal to their works being partly filled with scrap iron; my experiments showed me, however, that this method of purification was not so efficient as that by "polarite."

On looking over the results of the analysis of the water of the Bahr-Yousef, it has struck me that the apparent exception in July (see Table VII) may seem to contradict the conclusion I have drawn that the water of the Nile purifies itself during its flow; a glance at the conditions of the Bahr Yousef will make it plain that this is but an apparent exception. In June the Nile is at its worst; it is directly afterwards flushed by the flood; as the Bahr-Yousef empties itself into the Birket-el-Kûm, which has no apparent outlet, a rapid flow of water cannot take place; the effect of the flood is to push down gradually the water that is in it. We should expect then to find the June bad water to occur at a later date in the Bahr Yousef, and it is probably the bad water found at Assiout in June, which makes the coefficient of purity high in July at Medinet-el-Fayoum. The same conditions obtain at

Deyrout; this town is, however, much nearer Assiout, and has part
of the water taken away by the Ibrahimieh Canal. I think that
it would be correct to compare the water at Deyrout with that
at Assiout a week beforehand, and that at Medinet-el-Fayoum
with that a month before at Assiout. This should be noted in
future researches.

IV. THE WATER OF THE NILE CHEMICALLY CONSIDERED AS THE SOURCE OF FERTILIZERS IN EGYPT.

In the preceding portions I have made no reference to the sus-
pended matter. This I propose to do here.

The soil of Egypt is enriched by no artificial fertilizers, and
the mud of the Nile is its only supply of those constituents which
growing crops remove from the ground. Indeed, the soil of Egypt
has been formed from the mud of the Nile by its deposition during
the overflowing of its banks during past ages. I had first intended
to study variations in composition of the mud, but soon finding
that the laws governing the variations in the quantity of the sus-
pended matter were very imperfectly understood, I relegated my
first idea to the future, and devoted what time was at my dis-
posal to the study of these laws.

As the question of sampling was here very important I felt
obliged to take the samples myself and had to devote a consid-
erable time to traveling on the Nile for this purpose.

All samples were taken with the apparatus figured, which
consisted of a funnel shaped jar A closed at one end by a cork B
to which was firmly riveted a metal plate one and a half mm. in
thickness, and which was covered with sealing wax over its
whole surface; through this cork, and soldered to the plate
passed the tap C; at the other end the tap C_1, was fixed by
means of a piece of India rubber tubing, and held in place by
being bound round with wire to two pieces of wood placed on
each side; to the taps C and C_1, were fixed arms D and D_1, which
were connected by the rod E, weighted by the weight F; a cord
was attached to the upper end of E, and by pulling this the two
taps could be opened simultaneously, and on releasing it the
weight F caused them to close; the whole apparatus was sus-
pended from the rope H by a net-work of cords which encircled
the vessel A, and terminated in the rope J, from which hung

the weight G ; the capacity of the apparatus was two and a half liters.

It was used as follows: After being lowered to the required depth, the taps were opened by pulling the cord attached to E, the water entered by C_1, and the air escaped by C ; when no more bubbles of air could be seen rising, the cord was released, and the apparatus withdrawn; the water was then transferred to a bottle.

The shape of the apparatus was chosen in order to facilitate the escape of all the suspended matter in the bottle.

This apparatus was also used for sounding and measuring the difference of velocity between the surface and bottom of the river, as the bubbles practically always rose in a straight line. It was assumed that the difference between surface and bottom velocity was inappreciable.

Experiments were first made to determine whether the amount of suspended matter in different parts of the river was substantially the same or not.

In the first series samples were taken in the center of the river (a) at the surface, (b) at the bottom and (c) midway with the following results: Suspended matter, (a) 176.95 ; (b) 194.64 ; (c) 188.64.

In the second a mean sample was taken, (d) in the middle of the river, and (e) as near the banks as possible, with results as follows : Suspended matter, (d) 147.66 ; (e) 157.35.

The velocity was in both cases about four miles an hour.

These results showed that differences did exist in different parts of the river, but that they were not serious; except, perhaps, at the surface the difference does not exceed five per cent. All samples analyzed were mixtures of water from at least four different parts of the river, and may fairly be considered as average samples.

As the difference is shown to be small, the results in Tables I, II, and III may be taken into consideration, and will be discussed later on.
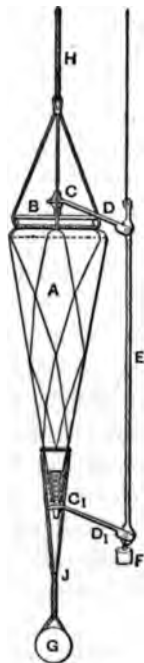
In Table XII are given the results of the determinations of suspended matter in the water at Kasr-el-Nil at short intervals, together with the height of the Nile at Assouan, the approximate velocity deduced from the time taken by the water to flow from Assouan to Cairo (information supplied by the Chief Inspector of Irrigation), and the velocity at Kasr-el-Nil calculated from the amount of suspended matter by the formula given below.

In Table XIII are the results of the analysis of corresponding samples of water at Assouan, Beni-Souef, Wasta, Atfeh, Helouan and Kasr-el-Nil; in Table XIV the results of analysis of corresponding samples at Assiout, Minieh, Beni-Souef, and Kasr-el-Nil; and in Table XV the analysis of corresponding samples at Wady Halfa and Kasr-el-Nil. The samples at Wady Halfa and Assouan are not mean samples, but were taken at half a meter below the surface, and the results should therefore be increased by about five per cent., but this does not affect the conclusions drawn therefrom.

During one voyage up the Nile, I observed that at Maghagha the current at a certain part was only running at one and a half miles per hour ; at Manfalout finding a narrow creek, I ran my steam launch firmly aground, and by means of the propeller created an artificial current of ten miles an hour and a sample was taken after the lapse of some time ; these samples gave the following results on analysis :

Place.	Velocity.	Suspended matter.
Maghagha	1.5	21.72
Manfalout	10.0	953.6

From these I deduced the following formula, connecting the rate of flow and the amount of suspended matter : $S = 9.5 \ V^2$; where S is the suspended matter in parts per 100,000, and V is the velocity in miles per hour.

By means of this formula, I have calculated the velocity of the Nile at Kasr-el-Nil on the 15th, 22nd, and 28th of August and the 4th and 15th of September, in each case with satisfactory results, considering the very approximate way of estimating the velocity, except on the 15th of August ; various considerations, however, lead me to conclude that the velocity on that date at Kasr-el-Nil was greater than that stated, among which

I may enumerate : (a) the river was rising very rapidly, there being an increase in four days of one meter, and it is highly probable that with such a rapid rise, a somewhat greater current should be obtained; (b) under the Kasr-el-Nil bridge only a part of the river runs, there being another branch which conveys when the river is high, another part on the Guizeh side of Gezireh ; as the Nile was not very high on the 15th of August, it is probable that the bulk of the water traveled under the Kasr-el-Nil bridge, a comparatively narrow channel, and the actual velocity was by this slightly increased.

On the whole I think that the figures in Table XII confirm the formula.

It is necessary, in order that the formula hold that the following premises be granted : (a) that the density and surface tension of the mud (and therefore the size of particles) be constant ; (b) that the water be mixed throughout ; (c) that the water be saturated with mud.

Considering that the composition of the mud is, within very narrow limits, constant, premise (a) may be assumed to be correct ; of the practical correctness of the other two, my personal observations during my voyages on the Nile during its flood, have convinced me ; I noted especially the numerous currents and cross currents, the destruction of the banks, and their rapid absorption, the practical absence of much mud at the bottom of the river, and sundry smaller points.

The truth of the premises is indirectly confirmed by the agreement between the numbers found and calculated in Table XII.

TABLE XII. DETERMINATIONS OF SUSPENDED MATTER AT KASR-EL-NIL (CAIRO).

Date.	Height of Nile at Assouan.	Approximate velocity.	Suspended matter.	Calculated velocity.
August 1, 1891	87.35	2.5	29.80	....
" 11, 1891	90.44	3.85	98.48	....
" 15, 1891	91.43	3.85	188.64	4.46
" 22, 1891	92.24	3.85	134.30	3.78
" 28, 1891	92.44	3.85	160.44	4.09
September 4, 1891	92.61	3.85	147.66	3.94
" 15, 1891	92.87	3.85	151.64	3.99

I have also frequently observed that when the Nile mud is allowed to settle, it cakes after a lapse of time, and becomes difficult to remix with the water until after a certain amount of

force has been used to stir it up ; after being stirred up it is easy of absorption by the water until allowed to cake again.

On these observations I have founded the following theory : The suspended matter is brought down by the Blue Nile and the Atbara (and to a lesser extent by the White Nile), and has little tendency to deposit until the flow is checked ; this check occurs first and principally in Lower and Middle Egypt by the drawing off of the water into the canals and basins for the irrigation of the country, and it is there that the mud is principally deposited ; there is little tendency to deposit in Upper Egypt and farther south, as the velocity is to a much greater extent maintained during the depositing period ; the mud-carrying waters of the Blue Nile and the Atbara, having been diluted by the comparatively clear waters of the White Nile, the river is probably by no means saturated, and cannot become so in Upper Egypt and above during the flood, as there is no great store of deposited mud ; the deposited mud remains at the bottom and sides of the river during the period of low Nile and consequently low velocity, and cakes, thereby becoming a mass requiring a certain force given by a certain velocity (probably exceeding three miles an hour), to re-absorb it, and the water cannot become saturated till this "critical velocity" has been attained. On the attainment a rapid increase in the amount of suspended matter takes place in Middle and Lower Egypt until saturation is attained.

According to this theory the quantity of suspended matter should be during flood time actually greater in Middle and Lower Egypt than in Upper Egypt ; the correctness of the theory is borne out by the results in Tables XIII and XV, where it is shown that the Nile at Assouan and Wady Halfa contains considerably less suspended matter than the water at Cairo.

TABLE XIII. SUSPENDED MATTER AT ASSOUAN, BENI-SOUEF, WASTA, ATFEH, HELOUAN, AND CAIRO.

Date.	Place.	Height of Nile.	Suspended matter.
August 16, 1891	Assouan	92.15	104.90
" 27, 1891	Beni-Souef	92.21	141.83
" 22, 1891	Wasta	92.21	139.50
" 22, 1891	Atfeh	92.21	147.23
" 22, 1891	Helouan	92.21	143.59
" 22, 1891	Kasr-el-Nil	92.21	134.20

TABLE XIV. SUSPENDED MATTER AT ASSIOUT, MINIEH, BENI-SOUEF, AND CAIRO.

Date.	Place.	Height of Nile.	Suspended matter.
September 13, 1891	Assiout	92.87	149.82
" 14, 1891	Minieh	92.87	152.20
" 14, 1891	Beni-Souef	92.87	147.32
" 15, 1891	Kasr-el-Nil	92.87	151.67

TABLE XV. SUSPENDED MATTER AT WADY HALFA AND CAIRO.

Date.	Place.	Height of Nile.	Suspended matter.
August 15, 1891	Wady Halfa	92.44	112.10
" 28, 1891	Kasr-el-Nil	92.44	160.44

The results in Tables XIII and XIV show that the suspended matter is practically constant below Assiout, as is also the velocity; the water then is saturated here (*i. e.*, in Middle and Lower Egypt).

On the 1st and 11th of August, for which dates I have not calculated the velocity by the formula, the "critical velocity" had probably not been attained, and the water had not become saturated; premise (c) then does not hold, and therefore the formula would not be applicable.

My theory also explains the sudden increase of the suspended matter and its more gradual fall.

Although the suspended matter has its origin in the Blue Nile and Atbara (for the most part) the actual quantity in the Nile in Middle and Lower Egypt during flood time depends not on the amounts in these rivers, but on the velocity of the current.

Considering that my theory explains all the points concerning the amount of suspended matter in the Nile, it may be taken as generally true. The amount of suspended matter has no direct relation to the height of the Nile, but is dependent on the velocity, and it is a matter of extreme regret that I did not realize this at the time of making my experiments, or I should. have devoted my attention to the accurate determination of the velocity.

Dredgings were made of the bed of the river at Assiout, Minieh, Beni-Souef, Wasta, Atfeh, Bedrishen, old Helouan, Dar-el-Tin, Rodah, Guizeh, Guizeh Palace, and Kasr-el-Nil during the flood, and in each case the bed was found to consist chiefly of sand, with about five per cent. of mud and small quantities of the

magnetic oxid of iron mentioned above; samples were also taken just below the water and from the top of a small sand island formed by the Nile opposite Katr-el-Nabi, which had the same composition ; the formation of this island, and the presence in the sand as low as Cairo of the heavy magnetic oxid of iron, which occurs above Assiout, are striking examples of the force of the current.

I have made no detailed experiments on the variations of the composition of the mud ; the constituents valuable to agriculture are however practically constant in amount, and my conclusions as to the supply of mud may be taken as generally true as to the supply of fertilizers.

(V.) NOTES ON THE AGRICULTURE AND IRRIGATION OF EGYPT.

Egyptian agriculture is the mainstay of the country's prosperity, and the Nile is the mainstay of the agriculture. Fertilizers, as such, are not placed on the land, and the soil is dependent for its supply of the constituents annually removed by the plants in the mud brought and deposited by the Nile water. In former days the Nile was simply allowed to overflow its banks and inundate the country, the mud settled, and when the Nile fell again the clear water (mostly) drained off; this system is still followed in Upper Egypt, but in the remaining country the banks of the Nile have been raised and the water flows into canals, whence by a series of ramifications the water is allowed to pass on to the land. Looked at solely by the light of my theory the canal system is inferior to the older one, owing to the abundant opportunity for deposition of mud owing to the decreased velocity in the canals, and *the probable non-attainment of the " critical velocity "* in a very considerable portion of them.

This non-attainment of the " critical velocity " has a considerable importance ; the Nile bed is annually cleared out by the flow of the river, the canal beds are not, and therefore they are steadily rising and helping to diminish the supply of water, and therefore fertilizers to the land. Another difficulty is being felt; the level of the land is also rising, as it receives a slight addition yearly, and in lapse of time, it must be, and in some cases is,

too high for the proper flow of the water thereon. The Barrage was established in order to raise the height of the Nile, and to grapple with this difficulty. The difficulty is now again felt, and the proposals to grapple with it generally take the form of raising the height of the Nile by similar artificial structures. It is absolutely necessary not to lose sight of the fact that it is not large quantities of water that the land requires ; it is the mud contained in them, and the primary object, the amelioration of agriculture, will be defeated, if, although a much larger supply of water be given to the land, this water contain less mud.

In raising the height of the Nile, nothing must be done to in any part check its velocity, and attention must be paid to keeping up this velocity to the greatest possible extent in the canals ; it is better to be content with a much smaller quantity of water if it can be supplied with a great velocity, than to so raise the Nile as to allow enormous quantities of water to flow on the land at a very slow speed ; it is necessary to keep up the " critical velocity " in order to make the mud deposited during the period of slow velocity available at the necessary time.

I fully realize that there are enormous engineering difficulties, but at the same time my study of the Nile has revealed to me these points which are not fully realized ; it is beyond the scope of a chemist to discuss this question in more detail.

Wilcox's book on the irrigation system of Egypt gives very complete information on the engineering work of Egyptian irrigation.

(VI.) CONCLUSIONS AND SUGGESTIONS.

The conclusions from my work on the Nile are :

(1) The impurities in the Nile water are influenced by (a) the White Nile and analogous tributaries; (b) the Blue Nile and analogous tributaries ; (c) the impurities taken up during its flow ; (d) the self-purification it undergoes, of which (d) is the most important.

(2) The water of the Nile, at Cairo, is a moderate drinking water, and not an excessively bad one, as has been maintained ; after filtration through sand, as practised by the Cairo Water Company, not much exception can be taken

to it.   The Cairo Water Company's supply is on the whole
good.

(3) After filtration through "polarite" it becomes a most
excellent drinking water, fully equal and in many cases
superior to the water supplied to great English towns.

(4) The Nile in its downward flow takes up impurities both
mineral and those due to sewage ; these are, however, in-
significant when compared with the great bulk of water
and to the self-purification.

(5) The amount of nitric acid is remarkably small.

(6) The purification and deficiency of nitric acid are largely
due to the iron minerals in its bed (*e. g.*, magnetic oxid of
iron, ferrous silicate, etc.).

(7) The quality of the water is worst just before the annual
rise, and at its best just after the attainment of its maxi-
mum.

(8) The suspended matter, which supplies the fertilizers
necessary to the agriculture of the country, is not only
dependent on the quantity brought down by the Blue Nile,
etc., but also and more especially on the velocity of the river.

(9) Portions of the suspended matter become deposited on
the bed of the river, as the current slackens, and a certain
"critical velocity" is necessary to stir this up again, so
as to be again taken into suspension.

(10) After the "critical velocity" has been attained, the
water saturated with mud, the relation between suspended
matter (S) and velocity (V) is expressed by the formula
$S = 9.5 V^2$.

(11) After the water is saturated (which only occurs in Mid-
dle and Lower Egypt) the quantity of suspended matter
is greater than that found in the Nile in Upper Egypt and
above.

(12) Any diminution of the current of the river, and espec-
ially the prevention of the attainment of the "critical
velocity" at the proper time will cause a loss of suspended
matter and therefore a detriment to agriculture.

I can only look upon my work as preliminary to a thorough
investigation of the Nile in the future ; there are many points

to be determined (*e. g.*, the "critical velocity," the actual amount of fertilizers necessary, and the lowest safe velocity, the laws that govern the settling of the mud, and the purification of the water, the composition of both water and mud, and the part played by each constituent) and these I leave as a legacy to my successors.

As Egypt depends on the Nile, it is imperative for the Egyptian government to have the fullest information on the Nile at their disposal, in order to control the river so as to obtain the greatest possible benefit therefrom. My work was chiefly done at the Khedivial Laboratory, at Cairo, but I found that the rough laboratory that I fitted up on board the steam launch, No. 74, was of great assistance, and future investigation should be carried on in a laboratory of this description ; it would require a steamer large enough to hold thirteen or fourteen persons, and powerful enough to steam six miles against the full stream, and of low draught,—preferably a stern-wheeler.

At least five years should be devoted to the work, and the total expenses would be :

> Initial expenses £1650
> Five years, at £1903..................... 9515
>
> Total......................£11,165

The Egyptian government should be prepared to find that sum. A great deal of work could also be done on the minerals of Egypt at the same time.

My conclusion (12) is highly important to the irrigation service, and I recommend it to the notice of the Public Works Department.

This paper contains the substance of a report made by me to the Director of the Sanitary Administration.

In conclusion I must express my warmest and most grateful thanks to Dr. Hussein Off, third chemist in the Khedivial Laboratory for his aid ; the devoted way in which he worked with me, often far into the small hours of the morning, has contributed greatly to the completion of my work.

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND J. BIRD MOYER.

In a former communication we demonstrated by a sufficient number of carefully made experiments that mercury and bismuth could not be separated electrolytically in a nitric acid solution. This was in line with the observations of Smith and Saltar,[1] who proved conclusively that copper and bismuth could not be separated under analogous conditions, and further that the statement in regard to the separation of bismuth and lead was incorrect. Pursuing our original intention of studying the electrolysis of metals in the presence of free nitric acid we offer the following additional experience in this field of investigation. We naturally expected little trouble, and indeed met with very little in our efforts to separate

Mercury from Lead.

1. Ten cc. of mercuric nitrate solution (= 0.1150 gram of metallic mercury), one cc. of lead nitrate solution (= 0.0126 gram of lead dioxide), and twenty-five cc. of nitric acid of sp. gr. 1.3, were diluted to 175 cc. and electrolyzed with a current liberating 1.3 cc. of electrolytic gas per minute. The precipitated mercury weighed 0.1151 gram, and the lead dioxide equaled 0.0123 gram. An examination of the mercury did not reveal any admixed lead.

2. In this experiment the quantities of lead and mercury were the same as in 1; the volume of nitric acid was increased to thirty cc. while the current registered 1.8 cc. of electrolytic gas per minute. The mercury deposit weighed 0.1150 gram and the dioxide of lead equaled 0.0126 gram.

In three other experiments in which the volumes of the added nitric acid (sp. gr. 1.3) equaled five cc., ten cc., and fifteen cc., respectively, the precipitated mercury contained metallic lead in varying but very considerable amounts.

Mercury from Lead and Bismuth.

In our former communication we cited an outlined analysis of an alloy containing tin, mercury, lead, and bismuth by Classen in his *Quantitative Analyse durch Elektrolyse, dritte*

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[1] J. ANAL. APPL. CHEM., 7, 128.

Auflage, p. 147, and showed that if it were conducted as there directed the analyst would in the end have little bismuth to determine as it would have most certainly gone out in company with the mercury. Omitting tin, we subjected a nitric acid solution of the other three metals to the action of the current. The solution contained 0.1150 gram of mercury, lead equal to 0.0126 gram of dioxide, bismuth 0.0718 gram, and fifteen cc. of nitric acid (sp. gr. 1.3). The total dilution was 180 cc. The current liberated 1.7 cc. of electrolytic gas per minute. The deposited mercury weighed 0.1262 gram and the increase in weight of the anode was 0.0164 gram; bismuth was discovered at both poles. A second and a third experiment with increased volume of acid resulted similarly. We must, therefore, reject this course if a satisfactory separation is desired.

Silver from Lead.

The separation presented no particular difficulties when working with conditions analogous to those recorded in the two following experiments:

1. Ten cc. of silver nitrate solution (= 0.1028 gram of silver), one cc. of lead nitrate solution (= 0.0144 gram lead dioxide), and fifteen cc. of nitric acid (sp. gr. 1.3), with total dilution of 200 cc., were acted upon by a current generating 1.8 cc. of electrolytic gas per minute. The deposit of silver weighed 0.1023 gram, and the lead dioxide 0.0144 gram.

2. The conditions were similar to those in 1. The precipitated silver weighed 0.1028 gram, and the lead dioxide 0.0145 gram.

Copper from Cadmium.

This separation was long since satisfactorily made by Smith. Classen met with similar results (*Berichte*, 17, 2473). Those interested will find Smith's description of the method[*] fully given in the *American Chemical Journal*, 2, 41. The results we append confirm those obtained by Smith in every particular.

1. Ten cc. of a copper sulphate solution (= 0.1341 gram of copper), five cc. of cadmium nitrate solution (= 0.1 gram of cadmium), and five cc. of nitric acid (sp. gr. 1.2), with total dilution of 200 cc., were electrolyzed with a current

that gave 0.6 cc. of electrolytic gas per minute. The precipi-
tated copper weighed 0.1346 gram; it contained no cadmium.

2. With conditions similar to those in 1, the precipitated cop-
per weighed 0.1341 gram. The current gave 0.6 cc. of electro-
lytic gas per minute.

Copper from Zinc.

The quantities of metal were equal; the volume of nitric acid
was five cc. (sp. gr. 1.3), total dilution 200 cc., and the current
gave one cc. of electrolytic gas per minute. The precipitated
copper weighed 0.1345 gram instead of 0.1341.

Copper from Zinc, Cobalt, and Nickel.

The quantities of metal were equal; the volume of nitric acid
(sp. gr. 1.3) was five cc., and the total dilution 200 cc. The
current registered 0.4 cc. of electrolytic gas per minute. The
precipitated copper weighed 0.1339 gram.

Copper from Iron and Zinc.

The metals were equal in quantity. The volume of nitric
acid was five cc. (sp. gr. 1.3). The current gave 0.7 cc.
of electrolytic gas per minute, while the dilution was the
same as in the preceding separations. The metal deposit
weighed 0.1340 gram.

The copper obtained in each of these separations was exam-
ined for the metals associated with it in solution, but they were
not found present. We may say here that we claim nothing
new in these separations of copper from zinc, nickel, cobalt, and
iron. They have been performed by others, but we merely offer
our results and the conditions under which they were obtained
as guides for any who may have occasion to make such separa-
tions.

Bismuth from Cadmium.

1. Five cc. of bismuth nitrate solution (= 0.0718 gram of
metallic bismuth), five cc. of cadmium nitrate solution (= 0.1
gram of cadmium), and fifteen cc. of nitric acid (sp. gr. 1.1)
were diluted to 180 cc. and electrolyzed with a current liberating
1.6 cc. of electrolytic gas per minute. The precipitated bis-
muth weighed 0.0716 gram instead of 0.0718 gram.

2. The conditions in this experiment were analogous to those
in 1, except that no additional acid was added to the nitric acid

solution of the two metals. The precipitated bismuth weighed 0.0719 gram.

Bismuth from Zinc.

0.0718 gram of bismuth, 0.1 gram zinc in the presence of two cc. of nitric acid (sp. gr. 1.3), with total dilution of 200 cc., gave 0.0712 gram of bismuth to a current setting free 0.4 cc. of electrolytic gas per minute. The anode was slightly discolored; its increase in weight was 0.0003 gram.

In a second trial with 1 cc. of additional acid the precipitated bismuth weighed 0.0717 gram. We can therefore regard this separation as satisfactory.

Bismuth from Nickel.

1. 0.0718 gram of bismuth, 0.1 gram of nickel, in the presence of two cc. of nitric acid (sp. gr. 1.3), were diluted to 180 cc. with water. A current liberating 0.5 cc. of electrolytic gas per minute acted upon this solution. The precipitation of bismuth was complete; the metal deposit weighed 0.0724 gram.

2. In this trial the quantities of the metals equaled those given in 1; the total dilution was 200 cc.; the volume of nitric acid of sp. gr. 1.3 equaled three cc., and the current gave 0.2 cc. of electrolytic gas per minute. The precipitated bismuth weighed 0.0716 gram.

A third experiment with conditions exactly like those of 2 gave 0.0716 gram of bismuth. The latter contained no nickel, and there was no deposit upon the anode.

Bismuth from Cobalt.

The quantities of metal were 0.0718 gram of bismuth and 0.1 gram of cobalt; the nitric acid (sp. gr. 1.3) equaled three cc., and the current gave 0.2 cc. of electrolytic gas per minute. The deposit of metallic bismuth weighed 0.0714 gram and there was also a very slight discoloration of the anode.

Other trials showed that the separation was possible.

It may be of interest to show what results were obtained when mixtures of the preceding metals were electrolyzed.

Bismuth from Zinc, Cobalt, and Nickel.

1. 0.0718 gram of bismuth, 0.1 gram of zinc, 0.1 gram of cobalt and 0.1 gram of nickel were mixed with two cc. of nitric

acid (sp. gr. 1.3), diluted to 200 cc., and acted upon by a current liberating 0.8 cc. of electrolytic gas per minute. The precipitated bismuth weighed 0.0739 gram, and upon examination showed the presence of both nickel and cobalt. The anode was covered with a blue coating.

A second, third, and fourth trial, with conditions almost identical with those in the preceding example, showed the presence of 0.0729 gram, 0.0738 gram, and 0.0739 gram of bismuth, which in each instance was contaminated with cobalt and nickel.

Bismuth from Cobalt and Nickel.

Zinc was omitted, and by employing the remaining three metals in the amounts given in the preceding experiment, using three cc. of nitric acid of sp. gr. 1.3, and acting upon the mixture after dilution to 200 cc. with a current liberating 0.3 cc. of electrolytic gas per minute, the bismuth that was precipitated weighed 0.0736 gram. It contained nickel.

Bismuth from Cobalt and Zinc.

0.0718 gram of bismuth and 0.1 gram each of cobalt and zinc were mixed with two cc. of nitric acid of sp. gr. 1.3, diluted to 180 cc. with water, and electrolyzed with a current giving 0.6 cc. of electrolytic gas per minute. The bismuth weighed 0.0747 gram; it contained cobalt, and the anode was covered with a film of oxide.

Bismuth from Cobalt, Nickel, and Zinc.

Using the same quantities of metals as given in the preceding experiments we increased the volume of added acid to five cc. The deposit of bismuth weighed 0.0728 gram and contained both cobalt and nickel.

Upon making a trial with the following conditions we were successful in effecting the separation with all the metals present: 0.0718 gram bismuth, 0.1 gram zinc, 0.1 gram cobalt, 0.1 gram nickel, eight cc. of nitric acid of sp. gr. 1.3, total dilution 200 cc., and a current that gave 0.4 cc. of electrolytic gas per minute. The deposit of bismuth weighed 0.0718 gram. It did not show the presence of any other metal upon examination. In this separation there was no discoloration of the anode. Subsequent experiments were equally successful in the

separation, although in several of them the anode was slightly discolored; its weight, however, was not increased more than 0.0004 gram.

We may add that the bismuth was deposited upon platinum dishes weighing from sixty to seventy grams. The metal deposit was, in all those trials that approached success, adherent and regular in appearance. It was washed with warm water, alcohol, and ether. The strength of current indicated in all the experiments given in this communication were with voltameter and electrolyte in circuit.

While the separation of bismuth from the various metals mentioned is possible if the conditions we have worked out are preserved, we cannot fail to observe that the solution in nitric acid is not nearly so satisfactory as that in which the metals exist as sulphates together with free sulphuric acid. With this last solution Smith and Knerr[1] obtained very excellent results.·

CHEMICAL LABORATORY OF
THE UNIVERSITY OF PENNSYLVANIA,
APRIL 27, 1893.

A RAPID METHOD FOR THE TECHNICAL ANALYSIS OF BLAST FURNACE SLAG.

BY OSCAR TEXTOR.

The composition of the slag furnishes a valuable guide to the blast furnace manager in operating his furnace. Analyses of ore, limestone, and coke may be misleading, when the samples tested are not properly taken and do not represent an average quality of the raw materials in the stock piles. The products of the furnace, the pig iron and the slag, must, however, show what is being put into the furnace, hence a knowledge of their composition is desirable.

Determinations of silica and alumina taken together are the only regular tests made by some furnace men; the percentages of lime and magnesia on the other hand are the criterion by which another manager operates. The sulfur determination, though usually considered unimportant, really furnishes an index as to the quality of the coke. In the laboratory of the Cleveland

Rolling Mill Company, the five determinations are made daily. The demand for a rapid method hereby created was filled by the development of a process which enables a chemist, with the usual laboratory appliances, to make an analysis easily in two hours, whereas, with the aid of some special apparatus, the five determinations have been completed in our laboratory in less than one hour.

The procedure to be described contains only a few new features; in the main it is the application of well known methods and operations. Instead of determining the silica, alumina, lime, and magnesia in one sample, two portions are weighed. The operations will be given in the order in which they are performed to secure speed. What may seem like unnecessary detail is introduced, because the rapidity of the work depends in part upon these minor points.

For sulfur weigh 0.5 gram into an ordinary tumbler, as this is less liable to be broken by a stirring rod, than a beaker. For silica and alumina, 0.5 gram is taken and transferred to a pint beaker marked SiO_2. For lime and magnesia, 1.325 grams are put into a pint beaker which is marked CaO.

Into the two pint beakers introduce twenty to twenty-five cc. of hot water; give the liquid a rotary motion to stir up and evenly distribute the slag; bring rapidly to a boil over a bare light; add to the beaker marked SiO_2 ten cc. of dilute hydrochloric acid (1 : 1) and keep the liquid in motion till the fine slag particles are dissolved. If the liquid is not kept in motion, the acid liberates gelatinous silica, which surrounds small particles of slag rendering decomposition difficult, and the silica and the included slag adhere to the bottom of the beaker. If properly added, the acid produces a clear or slightly turbid solution, the turbidity usually present being due to finely divided, insoluble, suspended matter, free sulfur, or carbon.

The beaker marked CaO is treated in the same manner, with this difference, that fifteen to twenty cc. of hydrochloric acid (1 : 1) are added instead of ten cc. The two beakers are boiled until the slag is dissolved. The solution in the beaker marked SiO_2 is evaporated as low as safety will permit over the bare light, two or three drops of nitric acid added, and the beaker stood on

the iron plate, where it is left until all visible signs of moisture disappear, when it is transferred to a previously heated asbestos board. A strong heat is continued till •the residue is dry or hydrochloric acid fumes can no longer be detected.

While this evaporation of the silica and alumina solution is going on, the lime and magnesia beaker is removed from the light, fifteen cc. of strong hydrochloric acid containing four or five drops of nitric acid are poured in while the solution is still hot; the nitric acid oxidizes the ferrous iron readily with heat. Pour in cold water up to 300 or 350 cc., stir; add slowly, five cc. at a time, twenty-five cc. of strong ammonium hydroxid. This precipitates silica and alumina. The ammonium hydroxid must be added slowly in small portions, so that some ammonium chlorid may be formed to hold the magnesia in solution and prevent its precipitation with silica and alumina. Pour the liquid with precipitate into a flask marked on the neck at 530 cc., fill to the mark and mix. Filter through a large dry paper in a five inch ribbed funnel, and collect the filtrate in a 250 cc. graduated cylinder. The first 250 cc. of filtrate, representing 0.625 gram of slag, transfer to a pint beaker marked MgO, using not more than ten or fifteen cc. of wash water to rinse out the cylinder. The next 200 cc. of filtrate, representing 0.5 gram of slag is poured into a beaker marked CaO. Bring the contents of both beakers to a boil, add to the magnesia portion twenty-five cc. of a saturated solution of ammonium oxalate and twenty cc. of the same reagent to the lime portion, stir each a few seconds, then place the magnesia beaker in water to cool. The calcium oxalate precipitate is filtered off at once, washed well with hot water, the filter spread out on the side of the beaker in which the precipitation was made, the calcium oxalate washed from the paper, dissolved in hot water containing fifteen cc. of strong sulfuric acid, and the solution titrated with potassium permanganate. When the beaker containing the magnesia solution is cool, pour its contents into a flask with a 300 cc. mark on the neck, fill to the mark and mix by pouring back into the beaker and stirring. Filter through a heavy dry paper in a five inch ribbed funnel; 240 cc. of the filtrate, representing 0.5 gram of slag, are poured into a pint beaker, into which there has previously been

put ten cc. of sodium phosphate solution (thirty grams to 250 cc.) and ten or fifteen cc. of strong ammonium hydroxid; or, use an Erlenmeyer flask instead of a beaker. Agitate for ten minutes to precipitate the magnesia, with a shaking machine if a flask was used, or by blowing air through the liquid by means of a blast arrangement, if the beaker is used for the precipitation.

By this time the silica and alumina residue has become thoroughly dry, the beaker is removed from the light, and in order to avoid breaking by standing the glass on the cool table, and yet have the cooling proceed rapidly and safely, the beaker is suspended by means of a wire beaker holder. When cool, about fifteen cc. of strong hydrochloric acid is poured on the residue, and the beaker replaced on the hot asbestos board. The magnesia precipitate is now filtered, and washed as usual with weak ammonia water. The wet filter containing the phosphate is placed in a crucible, and put over a Bunsen flame, only the point of the flame touching the crucible; this dries and chars the filter rapidly. When the paper is partly charred, cool the crucible, shake out the precipitate into the bottom, put the paper back also and replace over the full Bunsen flame. By this procedure the precipitate is quickly burned to a clean white residue.

The silica beaker with the hydrochloric acid has now stood on the hot asbestos board for three to five minutes; add twenty-five cc. hot water and let the solution boil over an open flame for another minute. Filter though an ashless, nine cm. paper, supplied with a platinum cone or tip. After the liquid has run through rinse the silica from the beaker into the funnel. Do not at this point use a rubber to remove the particles adhering to the beaker, but pour hot water into the beaker, give it a whirling motion and run it into the filter. Repeat this four or five times using enough water each time to fill the filter. The alumina is now all contained in the filtrate which is placed over the open flame to boil. The silica is cleaned out of the beaker with a rubber and as the finely divided precipitate now clogs the pores of the paper, suction may be applied to hasten filtration. More washing of the silica is unnecessary and the wet paper is put into a crucible and ignited.

When the alumina solution begins to boil, add strong ammonium hydroxid in excess, a few cc. at a time, stirring well after each addition in order to form ammonium chlorid to prevent the precipitation of magnesia. Filter immediately, without suction at first, through an ashless paper eleven cm. in diameter and supplied with a platinum tip. If the filter is thick and the funnel a good one, the filtration proceeds rapidly at the outset. When the last portion of the liquid has almost all passed through the paper, apply suction, which is increased and continued till the precipitate becomes shrivelled and furrowed over its whole surface. Perhaps a minute is required for this to take place. The washing will now proceed rapidly, as the bulky and slimy precipitate has been contracted to a small volume by the strong and continued suction. Four or five times filling of the filter with hot water suffices for the washing. Ignite and weigh as alumina. As the slag usually contains but low percentages of iron, this element is weighed with the alumina, and the whole reported as such. But the iron may be rapidly determined by dissolving one gram of slag in the manner indicated, using fifty to seventy-five cc. of water, boiling to expel hydrogen sulfid, adding one or two drops of stannous chlorid, cooling, adding mercuric chlorid and manganous sulfate solutions, and titrating with potassium permanganate.

To the 0.5 gram weighed for sulfur add about 150 cc. hot water and some starch solution. Now add about fifteen cc. of an iodin solution representing 0.01 per cent. of sulfur in each cc., when five grams of substance are taken, then fifteen to twenty cc. of strong hydrochloric acid and stir. The slag soon dissolves with a little stirring ; the hydrogen sulfid liberated is oxidized by the iodin solution, which is added to the end reaction. One cc. of iodin equals 0.1 per cent. sulfur when 0.5 gram of substance is taken.

The small amount of manganese present in the slag is not determined ; it appears in part in the magnesium pyrophosphate residue.

The potassium permanganate solution is made by weighing out 13.0335 grams potassium permanganate into a dry five pint acid bottle, then adding 2300 cc. water. One cc. of this solu-

tion equals two per cent. of lime when 0.5 gram of substance is taken. The solution is standardized with an oxalic acid solution containing 3.818 grams oxalic acid in 500 cc. water; twenty cc. of the oxalic solution equal 13.9 potassium permanganate solution.

THE MANUFACTURE OF NITROGLYGEROL.

By P. Gerald Sanford, F. I. C., F. C. S.

Every one employed in the buildings should wear list or sewn leather shoes, which of course must be worn in the buildings only; the various houses should be connected with paths laid with cinders, or boarded with planks, and any loose sand about the site of the works should be covered over with turf, or cinders, to prevent its blowing about and getting into the buildings. It is also of importance that stand pipes should be placed about the works with a good pressure of water, the necessary hose being kept in certain known places where they can be at once got at in the case of fire, such as the danger area laboratory, the foreman's office, etc. It is also desirable that the above precautions against fire should be tested once a week. With regard to the heating of the various buildings in the winter, steam pipes only should be used; and should be brought from a boiler house outside the danger area, and should be covered with kieselguhr, or fossil meal and tarred canvas; these pipes may be supported upon poles. A stove of some kind should be placed in the corner of each building, but it must be entirely covered in with woodwork, and as small a length of steam pipes should be within the building as possible. In the case of a factory where nitroglycerol and dynamite are manufactured, it is necessary that the workpeople should wear different clothes upon the danger area to those worn usually, as they are apt to become impregnated with nitroglycerol, and thus not very desirable, or safe, to wear outside the works; it is better also that these clothes should not contain any pockets, as this lessens the chance of matches or steel implements being taken upon the danger area. Changing houses, one for the men, and another for the girls, should also be provided. The tools used upon the danger area should when-

ever the building is in use, or contains any explosive, be made of phosphor bronze or brass, and brass nails or wooden pegs should be used in the construction of all the buildings.

<div align="center">MANUFACTURE.</div>

Nitroglycerol is prepared upon the manufacturing scale by, gradually adding glycerol to a mixture of nitric and sulfuric acids, of great strength. The mixed acids are contained in a lead vessel, which is kept cool by a stream of water continually passing through worms in the interior of the nitrating vessel, and the glycerol is gradually added in the form of a fine stream from above. The manufacture can be divided into three distinct operations, *viz.*, nitration, separation, and washing, and it will be well to describe the various operations in this order.

Nitration.—The most essential condition of nitrating is the composition of the mixed acids; the best proportions have been found to be three parts by weight of nitric acid, of a specific gravity 1.525 to 1.530, and containing as small a proportion of the oxids of nitrogen as possible, to five parts of sulfuric acid of a sp. gr. of 1.84 at 15° C. and about 97 per cent. sulfuric acid. It is of the very greatest importance that the nitric acid should be as strong as possible ; nothing under a gravity of 1.52 should ever be used, even to mix with stronger acid, and the nitration results will be proportional to the strength of the acid used. It is also of great importance that the oxids of nitrogen should be low, and they should be kept down to as low as one per cent., or even lower. It is also desirable that the nitric acid should contain as little chlorin as possible. The following is the analysis of a sample of acid which gave very good results: Specific gravity, 1.525; N_2O_4, 1.03 per cent.; nitric acid, 95.58 per cent.

The amount of real nitric acid, and also the nitric peroxid present should always be estimated, as the specific gravity is not a sufficient guide to the strength of the acid, as an acid having a high gravity, due to some three or four per cent. of nitric oxid in solution, will give very poor results in nitrating. A tenth normal solution of sodium hydroxid, with phenolphthalein as indicator, will be found the most convenient method of estimating the total acid. The following method is very quick and reliable: Weigh a 100 cc. flask containing a few cc. of distilled water, and then

add, from a pipette, one cc. of the nitric acid, and reweigh (this will give the weight of acid taken); now make up to 100 cc. at 15° C., shake well, and take out ten cc. with a pipette, drain into a small Erlenmeyer flask, and add a little phenolphthalein and titrate with the tenth normal soda solution. The nitric peroxid can be estimated with a solution of potassium permanganate of $\frac{N}{10}$ strength, thus: Take a small Erlenmeyer flask containing about ten cc. of water, and add from a burette ten to sixteen cc. of the permanganate solution, then add two cc. of the acid to be tested, and shake gently, and continue to add permanganate solution as long as it is decolorized, and until a faint pink color is permanent.

Example: $\frac{N}{10}$ permanganate, 3.16 gm. per liter, 1 cc. $= 0.0046$ gm. N_2O_4. 2 cc. of sample of acid, sp. gr. 1.52 $= 3.04$ gm. taken for analysis. Took 20 cc. of the permanganate solution. $0.0046 \times 20 = 0.092$ gm. N_2O_4 and $\frac{0.092 \times 100}{3.04} = 3.02$ per cent. N_2O_4.

The specific gravity should be taken with an hydrometer that gives the gravity directly, or if preferred the two cc. of acid may be weighed.

It has been proposed to free the nitric acid from the oxids of nitrogen by blowing compressed air through it, and thus driving the gases in solution out. The acid was contained in a closed lead tank, from which the escaping fumes were conducted into the chimney shaft, and on the bottom of which was a lead pipe, bent in the form of a circle, and pierced with holes, through which the compressed air was made to pass; but the process was not found to be of a very satisfactory nature, and it is certainly better not to allow the formation of these compounds in the manufacture of the acid, in the first instance. The sulfuric acid used should contain from 96.5 to 97 per cent. of sulfuric acid, and be as free as possible from impurities. Having obtained the nitric and sulfuric acids as pure as possible, the next operation is to mix them. This is best done by weighing the carboys in which the acids are generally stored before the acids are drawn off into them from the condensers, and keeping their weights constantly attached to them by means of a label; it is then a simple matter to weigh off as many carboys of acid, as may be required for any number of mixings, and subtract the weights of the carboys. The two

acids should, after being weighed, be poured into a tank and mixed, and subsequently allowed to flow into an acid egg, or montejus, to be afterwards forced up to the nitrating house in the danger area. The montejus, or acid egg, is a strong cast iron tank of either an egg shape, or a cylinder, with a round end. If of the former shape, it would lie on its side, and upon the surface of the ground, and would have a manhole at one end, upon which a lid would be strongly bolted down; but if of the latter shape the lid of course is upon the top, and the montejus itself is let into the ground. In either case the principle is the same; one pipe, made of stout lead goes to the bottom, and another just inside to convey the compressed air, the acids flowing away as the pressure is put on, just as blowing down one tube of an ordinary wash bottle forces the water up the other tube to the jet. The pressure necessary will of course vary immensely, and will depend upon, the height to which the acid has to be raised and the distance to be traversed. The mixed acids having been forced up to the danger area and to a level higher than the position of the nitrating house, should before being used, be allowed to cool, and leaden tanks of sufficient capacity to hold at least enough acid for four or five nitrations should be placed in a wooden house upon a level at least six or seven feet above the nitrating house. In this house also should be a smaller lead tank, holding, when filled to a certain mark, just enough of the mixed acids for one nitration; the object of this tank is, that as soon as the man in charge knows that the last nitration is finished, he refills this smaller tank (which contains just enough of the mixed acids), and allows its contents to flow down into the nitrating house, and into the nitrator, ready for the next nitration.

The nitration is usually conducted in a vessel constructed of lead, some four feet wide at the bottom, and rather less at the top, and about four feet or so high; the size of course depends upon the volume of the charge it is intended to nitrate at one operation, but it is always better that the tank should be only two-thirds full. A good charge is sixteen cwt. of the mixed acids, in the proportion of three to five; that is, six cwt. of nitric acid, and ten cwt. of sulfuric acid and 247 pounds of glycerol.

Upon reference to the equation showing the formation of nitroglycerol it will be seen that for every one pound of glycerol 2.47 lbs. of nitroglycerol should be furnished[1] but in practice the yield is only about two and one-fourth lbs., the loss being accounted for by the unavoidable formation of some of the lower nitrates of glycerol, which are dissolved and thus washed away. The lead tank is generally cased in wood-work, with a platform in front for the man in charge of the nitrating to stand upon, and whence to work the various taps. The top of the tank is closed in with a dome of lead, in which is a small glass window, through which the progress of the nitrating operation can be watched. From the top of this dome is a tube of lead which is carried up through the roof of the building; it serves as a chimney to carry off the acid fumes which are given off during the nitration. The interior of this tank contains at least three concentric spirals of at least one-inch lead pipe, through which water can be made to flow during the *whole* operation of nitrating; another lead pipe is carried through the dome of the tank, as far as the bottom, where it is bent round in the form of a circle; through this pipe, which is pierced with small holes, about one inch apart, compressed air is forced at a pressure of about sixty lbs. in order to keep the liquids in a state of constant agitation during the whole period of nitration. There must also be a rather wide pipe, of say two inches internal diameter carried through the dome of the tank, which will serve to carry the mixed acids to be used in the operation. There is still another pipe to go through the dome, *viz.*, one to carry the glycerol into the tank; this need not be a large bore pipe, as the glycerol is generally added to the mixed acids slowly. Before the apparatus is ready for use, it requires to have two thermometers fixed, one long one to reach to the bottom of the tank, and one short one, just long enough to dip under the surface of the acids; when the tank contains its charge, the former gives the temperature of the bottom, and the latter of the top of the mixture. The glycerol should be contained in a small cistern, fixed in some convenient spot, upon the wall of the nitrating house, and should have a pipe let in flush with the bottom,

[1] Thus, if ninety-two lbs. glycerol give 227 lbs. nitroglycerol $\frac{227 \times 1}{92} = 2.47$ lbs.

and going through the dome of the nitrating apparatus; it must of course be provided with a tap, or stop cock, which should be placed just above the point where the pipe goes through the lead dome.   Some method of measuring the quantity of glycerol used must be adopted.   A gauge tube graduated in inches is a very good plan, but it is essential that the graduations should be clearly visible to the operator upon the platform in front of the apparatus.   A large tap made of earthenware (and covered with lead) is fixed in the side of the nitrating tank just above the bottom, to run off the charge after nitration; this should be so arranged that the charge may be at option run down the conduit to the next house, or discharged into a drowning tank which may sometimes be necessary in cases of decomposition.

The drowning tank is generally some three or four yards long and several feet deep, lined with cement, and placed close outside the building.   The apparatus having received a charge of mixed acids, the water is started running through the pipes coiled inside the tank, and a slight pressure of compressed air is turned on, to mix the acids up well before starting.   The nitration should not be commenced, until the two thermometers register a temperature of 18° C.; the glycerol tap is then partially opened, and the glycerol slowly admitted, and the compressed air turned on full, until the contents of the apparatus are in a state of very brisk agitation.   A pressure of forty lbs. is about the minimum. If 247 lbs. of glycerol is the charge being nitrated, it will require thirty minutes to complete the operation; but the compressed air and water should be kept on for an additional ten minutes after this, to give time for all the glycerol to nitrate.   The temperature should be kept as low as possible.   The chief points to attend to during the progress of the nitration are:

1. The temperature registered by the two thermometers.

2. The color of the nitrous fumes given off (as seen through the little window in the dome of the apparatus).

3. The pressure of the compressed air, as seen from a gauge fixed upon the air pipe first before it enters the apparatus.

4. The gauge showing the quantity of glycerol used.

The temperature as shown by either of the thermometers should not be at any time higher than 25° C. If the temperature

rises much above this the glycerol should be at once shut off, and the pressure of air increased for some few minutes until the temperature falls, and no more red fumes are given off. The nitration being finished, the large earthenware tap at the bottom of the tank is opened, and the charge allowed to flow away down the conduit to the next building, *i. e.*, to the separator.

The nitrating house is best built of wood, and should have a close-boarded floor, which should be kept scrupulously clean and free from grit, and sand; a wooden pail and a sponge should be kept in the house, in order that the workman may at once clean up any mess that may be made, and a small broom should be handy in order that any sand, etc., may be at once removed. It is a good plan for the nitrator to keep a book in which he records the time of starting each nitration, the temperature at starting and at the finish, the time occupied, and the date and number of the charge, as this enables the foreman of the danger area, at any time, to see how many charges have been nitrated, and gives him other useful information conducive to safe working. The newly made charge of nitroglycerol, upon leaving the nitrating house, flows away down the conduit, either made of rubber pipes, or better still of woodwork, lined with lead and covered with lids made of wood (in short lengths) in order that by lifting them at any point, the condition of the conduit can be examined as this is of the greatest importance, and the conduit requires to be frequently washed out and the sulfate of lead removed. This sulfate always contains nitroglycerol, and should therefore be burnt in some spot far removed from any danger building or magazine, as it frequently explodes with considerable violence.

In works where the manufacture of nitroglycerol is of secondary importance, and some explosive containing only perhaps ten per cent. of nitroglycerol is manufactured, and where perhaps fifty or 100 lbs. of glycerol are nitrated at one time, a very much smaller nitrating apparatus than the one that has been already described, will be probably all that is required. In this case the form of apparatus shown in Figure 1 will be found very satisfactory. It should be made of stout lead (all lead used for tanks, etc., must be "chemically pure lead"), and

may be made to hold fifty or 100 lbs., as found most convenient. This nitrator can very well be placed in the same house as the
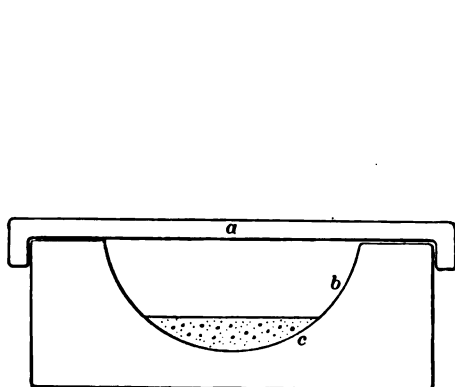
Section of Conduit.
a, lid.
b, lead channel.
c, cinders.

FIG. 1.

Small Nitrator.
T, thermometer.
W, windows.
P, water and air pipes.
P¹, glycerol pipe.
N, tap to draw off charge.

separator; in fact where such a small quantity of nitroglycerol is required, the whole series of operations of nitrating, separating, washing, etc., may very well be performed in the same building. It will, of course, be necessary to place the nitrator on a higher level than the separator, but this can easily be done by having platforms of different heights, the nitration being performed upon the highest. The construction of this nitrator is essentially the same as in the larger one, the shape only being somewhat different. Two water coils will probably be enough, and one thermometer. It will not be necessary to cover this form in with wood work.

Quite lately Edward Liebert has devised an improvement in the treatment of nitroglycerol. He adds ammonium sulfate or

ammonium nitrate to the mixed acids, during the operation of nitrating, which he claims destroys the nitrous acid formed, according to the equation :

$$(NH_4)_2SO_4 + 2HNO_2 = H_2SO_4 + 2N_2 + 4H_2O.$$
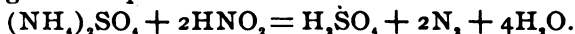
Separation.—The nitroglycerol, together with the mixed acids, flows from the nitrating house to the separating house, which must be on a lower level than the former. The separating house contains a large lead-lined tank, closed in at the top with a wooden lid, into which a lead pipe of large bore is fixed, and which is carried up through the roof of the building, and acts as a chimney to carry off any fumes. A little glass window should be fixed in this pipe in order that the color of the escaping fumes may be seen. The conduit conveying the nitroglycerol enters the building close under the roof and discharges its contents into the tank, which is only about two-thirds filled by the charge. There is in the side of the tank a small window of thick plate glass, which enables the workman to see the level of the charge, and also to observe the progress of the separation, which will take from thirty minutes to one hour. The tank should be in connection with a drowning tank, as the charge sometimes gets very dangerous in this building. It must also be connected by a conduit with the filter house, and also to the secondary separator by a conduit. The tank should also be fitted with a compressed air pipe, bent as in the nitrating apparatus. It should lay upon the bottom of the tank in the form of a loop. The
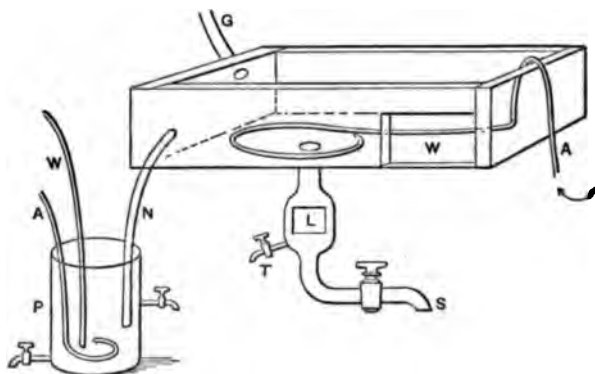
A. compressed air pipes ; G. Nitroglycerol enters ; N. Nitroglycerol leaves and enters P ; W. water pipe ; L. lantern window ; T, tap ; S, Nitroglycerol to second separator ; W, window in tank ; P, lead tank washing.

object of this is to mix up the charge in case it should get too hot through

decomposition. A thermometer should, of course, be fixed in the lid of the tank, and its bulb should reach down to the middle of the nitroglycerol (which rests upon the surface of the mixed acids, the specific gravity of the nitroglycerol being 1.6 and that of the waste acids 1.7; the composition of the acid mixture is now, nitric acid, eleven per cent., sulfuric acid, sixty-seven per cent., water, twenty-two per cent.), and the temperature carefully watched. If nothing unusual occurs, and it has not been necessary to bring the compressed air into use, and so disturb the process of separation, the waste acids may be run away from beneath the nitroglycerol, and allowed to flow away to the secondary separator, where any further quantity of nitroglycerol that they may contain separates out, after resting for some days. The nitroglycerol itself is run into a smaller tank, in the same house, where it is washed three or four times with its own bulk of water, containing about three lbs. of carbonate of soda, to neutralize the remaining acid. This smaller tank, should contain a lead pipe pierced, and coiled, upon the bottom, through which compressed air may be passed, in order to stir up the charge with the water and soda. After this preliminary washing the nitroglycerol is drawn off, into India rubber buckets, and poured down the conduit to the filter house; the wash waters may be sent down a conduit to another building, in order to allow the small quantity of nitroglycerol, that has been retained in the water as minute globules, to settle, if thought worth the trouble of saving; this of course will depend upon the usual out turn of nitroglycerol in a day, as little more than a bucket or so a week will be obtained when eight nitrations are performed a day.

Filtering and Washing.—The filter house, which must of course be again on a somewhat lower level than the separating house, must be a considerably larger building than either the nitrating or separating houses, as it is always necessary to be washing some five or six charges at the same time. Upon the arrival of the nitroglycerol at this house it first flows into a lead-lined wooden tank, containing a compressed air pipe, just like the one in the small tank in the separating house. This tank is half filled with water. and the compressed air is turned

on from half to a quarter hour. The water is then drawn off, and fresh water added. Four or five washings are generally necessary. The nitroglycerol is then run into the next tank, the top of which is on a level with the bottom of the first one. Across the top of this tank is stretched a frame of flannel, through which the nitroglycerol has to filter. This removes any solid matters, such as dirt or scum. Upon leaving this tank, it passes through a similar flannel frame across another tank, and is finally drawn off by a tap in the bottom of the tank into rubber buckets. The taps in these tanks are best made of vulcanite. At this stage, a sample of the nitroglycerol must be taken to the laboratory, and tested by the government heat test. If the sample will not pass the test, which is often the case, the charge must be re-washed for one hour, or some other time, according to the judgment of the chemist in charge. In the case of an obstinate charge, it

W, lead washing tank; W.P., water; S, nitroglycerol from separator; a, b, c, filter tanks; b_2, India rubber bucket.

is of much more avail to wash a large number of times with small quantities of water, and for a short time, than to use a lot of water and wash for half an hour. Plenty of compressed air should be used, as the compound nitric ethers which are formed are thus got rid of. As five or six charges are often in this house at one time, it is necessary to have as many tanks arranged in tiers, otherwise one or two refractory charges would stop the nitrating house, and the rest of the nitroglycerol plant. The chief causes of the nitroglycerol not passing the heat test are, either that the acids were not clean, or they contained objectionable impurities, or more frequently the quality of the glycerol used. The glycerol used for

making nitroglycerol should conform to the following tests:

(1) Minimum specific gravity at 15° C., 1.261.

(2) Should nitrify well.

(3) Separation should be sharp within half an hour without the separation of flocculent matter, nor should any white flocculent matter (due to fatty acids) be formed when the nitrated glycerol is thrown into water and neutralized with carbonate of soda.

(4) Should be free from lime and chlorin and contain only traces of arsenic, sulfuric acid, etc.

(5) Should not leave more than 0.25 per cent. inorganic and organic residue together when evaporated in a platinum dish without ebullition (about 160° C.) or partial decomposition.

(6) Silver test fair.

(7) The glycerol, when diluted one-half, should give no deposit or separation of fatty acids, when nitric peroxid gas is passed through it.

The white flocculent matter sometimes formed is a very great nuisance, and any sample of glycerol which gives such a precipitate when tried in the laboratory should at once be rejected, as it will give no end of trouble in the separating house, and also in the filter house, and it will be very difficult, indeed, to make the nitroglycerol manufactured from it pass the heat test. The out turn of nitroglycerol also will be very low. The trouble will show itself chiefly in the separating house, where the nitroglycerol in separating from the mixed acids will sometimes contain a large quantity of this white substance. Perhaps two or three inches will rise to the surface or hang about in the nitroglycerol, and will afterwards be very difficult to get rid of by filtration. The material appears to be partly an emulsion[1] of the glycerol, and partly some fatty acid, and as there appears to be no really satisfactory method of preventing its formation, the best plan is not to use any glycerol for nitrating that has been found by experiment upon the laboratory scale to give this objectionable matter. One of the most useful methods of testing the glycerol other than nitrating is to dilute a sample of the glycerol about one-half with water, and then passing a

[1] According to Mr. Otto Hehner.

current of nitrogen peroxid, N_2O_4, through it, when a flocculent precipitate of elaïdic acid (less soluble in glycerol than the original oleic acid) will be formed. Nitrogen peroxid is best obtained by heating dry lead nitrate (see Allen, *Commercial Analysis*, **2**, 301). The nitroglycerol, upon leaving the filter house, where it has been washed and filtered and has satisfactorily passed the heat test, is drawn off from the lowest tank in India rubber buckets, and poured down the conduit leading to the precipitating house, where it is allowed to stand for a 'day, or sometimes longer, in order to allow the little water it still contains to rise to the surface. In order to accomplish this, it is sufficient to allow it to stand in covered-in tanks of a somewhat conical form, and about three or four feet high. It can afterwards be drawn off in rubber buckets, when it will be of a pale yellow color, and should be quite clear. It is then ready for use in the preparation of dynamite, or any of the various forms of gelatin compounds, smokeless powders, etc., such as cordite, ballistite, and many others.

The Mixed Acids.—The mixed and waste acids from the separating house, from which the nitroglycerol has been as completely separated as possible, are run down the conduit to the secondary separator, in order to recover the last traces of nitroglycerol that it contains. The composition of the mixed acids after nitrating is generally somewhat as follows: Specific gravity, 1.7075 at 15° C.; sulfuric acid, 67.2 per cent.; nitric acid, 11.05 per cent.; and water, 21.7 per cent., with perhaps as much as two per cent. of nitric oxid, and, of course, varying quantities of nitroglycerol, which must be separated as it is *impossible* to run this liquid away, or to recover the acids as long as it still contains this substance. In order to do this, the mixture is run into large circular lead-lined tanks, covered in, and very much like the nitrating apparatus in construction; that is, they contain worms coiled round inside to allow of water being run through to keep the mixture cool, and a compressed air pipe in order to agitate the mixture if necessary. The top also should contain a window in order to allow of the interior being seen, and should have a leaden chimney to carry off the fumes which may arise from decomposition. It is also

useful to have a glass tube of three or four inches diameter substituted for about a foot of the lead chimney in order that the man on duty can at any time see the color of the fumes arising from the liquid. There should also be two thermometers, one long one reaching to the bottom of the tank, and one to just a few inches below the surface of the liquid.

The nitroglycerol, of course, collects upon the surface, and can be drawn off by a tap placed at a convenient height for the purpose. There will probably be never more than an inch of nitroglycerol at the most, and seldom that. It should be taken to the filter house and treated along with another charge. The acids themselves may either be run away or treated by a denitration plant of some kind. This house probably requires more attention than any other in the danger area on account of the danger of the decomposition of the small quantities of nitroglycerol, which, as it is mixed with such a large quantity of acids and water, is very apt to become hot, and decomposition, which sets up in spots where a little globule of nitroglycerol is floating surrounded by acids that gradually get hot, gives off nitrous fumes and perhaps explodes, and thus causes the sudden explosion of the whole. The only way to prevent this is for the workman in charge to look at the thermometers *frequently*, and at the color of the escaping fumes, and if he should notice a rise in temperature or any appearance of red fumes, to turn on the water and air and stir up the mixture, when probably the temperature will suddenly fall and the fumes cease to come off. The cause of explosions in this building is either the non-attention of the workmen in charge, or the bursting of one of the water pipes, by which means, of course, the water finding its way into the acids causes a sudden rise of temperature. If the latter of these two causes should occur, the water should at once be shut off and the air turned on full, but if it is seen that an explosion is likely to occur, the tank should be at once emptied by allowing its contents to run away into a drowning tank placed close outside the house, which should be about four feet deep, and some sixteen feet long by six feet wide ; in fact, large enough to hold a considerable quantity of water. But this last course should only be resorted to as a last

extremity, as it is extremely troublesome to recover the small quantity of nitroglycerol from the bottom of this large tank, which is generally a bricked and cemented excavation some few yards from the house. The heat test mentioned above is probably well known to all chemists who are connected with explosives. A full description of the method of working it, etc., will be found in the appendix to "The Explosives Act, 1875," a copy of which will be found in Eissler's *Modern Explosives*, p. 267.

When a sample of nitroglycerol is brought to the laboratory from the filter house it should first be examined to see that it is clear. It is also desirable to test it with a weak solution of Congo red, or methyl orange, to see if it is acid. If it appears to be decidedly alkaline it should be poured into a separating funnel and shaken with a little distilled water. This should be repeated, the washings (about 400 cc.) run into a beaker, a drop of Congo red or of methyl orange added, and a drop or so of $\frac{N}{2}$ hydrochloric acid added, when it should give with two or three drops at the most a blue color with the Congo red, or pink with the methyl orange, etc. The object of this test is to show that the nitroglycerol is free from soda, *i. e.*, that all the soda added to the charge in the separating house has been properly washed out, otherwise the heat test will show the sample to be better than it is.

Two points in the manufacture of nitroglycerol are of the greatest importance, *viz.*, the purity of the glycerol used, and the strength and purity of the acids used in the nitration. With regard to the first of these great care should be taken, and a complete analysis and thorough examination, including a preliminary nitration, should always be instituted. As regards the second, the sulfuric acid should be not only strong (about ninety-six per cent.) but as free from impurities as possible. With the nitric acid, which is generally made at the explosives works where it is to be used, care should be taken that it is as strong as possible (ninety-seven per cent. and upwards). This can easily be obtained if the plant designed by Mr. Oscar Guttmann[1] is used. The oxids of nitrogen *must* be as low

[1] *The Manufacture of Nitric Acid*, O. Guttmann, *J. Soc. Chem. Ind.*, *March*, *1893*.

as possible, and under one per cent.   It is also important that sulfates, chlorids, etc., should be absent.   It is hardly an exaggeration to say that success depends more upon the strength and purity of the nitric acid used than upon any other factor.

LABORATORY,
20 CULLUM STREET,
LONDON, E. C.

NOTE ON THE DETERMINATION OF SILICON BY DROWN'S METHOD.

BY ALLEN P. FORD.

In an article on "Discrepancy in Chemical Work by Different Workers," by Dr. C. B. Dudley, in the January number of THE JOURNAL OF ANALYTICAL AND APPLIED CHEMISTRY, I noticed one illustration he gave in particular.   It was a determination of silicon in a sample of steel, in which the result turned out by the Pennsylvania Railroad Company's laboratory was only one-half of that obtained by another chemist who worked on the same steel.   On looking into the matter to see where the trouble was, Dr. Dudley says he found that the chemist who had made the analysis in his laboratory had been taken away to attend to some other work, when the silicon determination had been evaporated to dryness and diluted with hot water, and consequently, instead of being filtered immediately, was allowed to stand in this condition forty-eight hours before being filtered and burned.   On making some test analyses subsequently on the same steel, he found it invariably lost about one-half on standing forty-eight hours, and more or less for a longer or shorter time.

Now this little instance was particularly interesting to me because I had frequently done the same thing—in fact, if I have to let a silicon determination stand a while before finishing it I prefer to bring it just to this point (the dry mass taken up in water acidified with hydrochloric acid) with no very good reasons perhaps except that it can dissolve in the meantime and be ready for filtering when I am ready to take it up, and I wondered if I had been making any such mistake as mentioned in the above named article when I did so. .

To satisfy myself I made some test analyses. As I did not have much time for experimental work, I had my assistant weigh out duplicate samples of any iron that he happened to be working on. One was run through without delay and the other was allowed to stand forty-eight hours, and in some cases longer, after evaporating to dryness and diluting. In no instance was the variation more than would be due to the error of manipulation. In some cases the one which had stood was a trifle the highest. These test analyses were made in ten or twelve different samples of steel and cast iron containing silicon varying from 0.1 per cent. in the steel to two per cent. in the highest cast iron.

Now it seems curious to me that our experiences should be so different. Is there some little difference in the details of the methods used which causes this discrepancy? I use Drown's method—at least it is that method in the main, for I have seldom seen the details given exactly alike in two different books. I do not dissolve the borings in a mixture of sulfuric acid and nitric acid, but prefer to dissolve in dilute sulfuric acid (1 : 5) and after complete solution, add strong nitric acid drop by drop until the effervescence ceases. Then again after evaporating to dryness I add a few drops of hydrochloric acid to the dry mass before dissolving in hot water. Whether these little details are observed in the laboratory of the Pennsylvania Railroad Company or not, I do not know, as it is not mentioned; and if not, is it possible that they would account for the partial solubility of the silica after long standing as noted in Dr. Dudley's article. If I had had time for experimenting and if I was certain of the exact method used by Dr. Dudley, I would have tried checks by it myself; but as it is, I will simply make this note and perhaps it will meet the eye of some one who has had more experience and can offer some explanation.

GRIFFIN CAR WHEEL CO.,
DETROIT, MICH., MAY 23, 1893.

A CONVENIENT AGITATOR, OR A SUBSTITUTE FOR THE SHAKING MACHINE USED IN THE PRECIPITATION OF PHOSPHORIC ACID.

BY OSCAR TEXTOR.

The writer has for some time utilized the air pressure obtained by a blast arrangement connected with a Richards filter pump for producing agitation in solutions of steel or pig iron from which the phosphorus is being precipitated as the yellow salt. After solution of the metal and oxidation by chromium trioxid or potassium permanganate, the molybdate is added to the beaker, in which the metal is dissolved, then the tube conveying the blast is introduced into the liquid and the quantity of air escaping regulated by a gas cock fitted to the air supply pipe. It is thus unnecessary to transfer the solution to a flask, and no further labor or attention is required after the blast is turned into the beaker. A cover glass prevents loss. Seven minutes suffice for a complete precipitation of phosphorus as the ammonium phosphomolybdate, though a shorter time might have the same effect; this is a point upon which no experiments have been made.

A, city water supply pipe; B, Richards filter pumps; C, ½-inch iron pipe conveying water and air into pipe D; D, 3-inch iron pipe in which water and air separate; E, exit of waste water into sewer; F, suction pipe leading to laboratory; G, blast pipe leading to laboratory.

The advantages of using this means of agitating are: That it requires no attention from the chemist; it continues its work uninterruptedly; it is simple in construction. At blast furnaces the blast pipe can be tapped and the air pressure obtained in that way.

Two Richards pumps will run eight determinations.

CADMIUM CHLORID AS AN ABSORBENT OF HYDROGEN SULFID.

BY FRANK L. CROBAUGH.

In many laboratories it has been the practice until recently to use two test tubes connected, containing an ammoniacal solution of a cadmium salt or an aqueous solution of a caustic alkali, for the absorption of the hydrogen sulfid from five grams of iron or steel. This method is still in use in several laboratories.

Some chemists fear incomplete absorption in this case, and make repeated tests for escaping sulfur at the exit for hydrogen. The practice has been to have three to four inches depth of liquid in the first tube and somewhat less in the second. The later substitution of one tube only to absorb the gas with from six to seven inches depth of liquid was regarded as hazardous at first. Finally, to expedite the work, a beaker was employed, which it was thought should contain at least three inches depth of absorbent.

In all cases ten to thirty times the amount of the active element theoretically necessary was used. Having witnessed this transition in several laboratories, and passed through it ourselves, we determined to find how little solution is necessary for complete absorption. To do this we employed fine drillings from one pig of No. 2 Bessemer metal, conceded by many chemists to contain 0.068 per cent. sulfur capable of being evolved.

The experiments were all made with these drillings and the same iodin solution in two consecutive days. The iodin solution was thoroughly matured before use and did not change appreciably from one day to the next. Cold hydrochloric acid (sp. gr. 1.10) was employed for the evolution. A gentle flame, gradually increased, was used immediately after the addition of sixty cc. of the acid to five grams of the drillings.

Using two tubes as above in three experiments, 8.9, 8.7, and 9 cc. of the iodin solution were required.

Using a beaker containing one and one-half inches depth of liquid, 8.6, 9, and 9 cc. were required.

Using a beaker containing one inch depth of liquid, 9 and 8.7 cc. were required.

In all of the above experiments ten cc. of ammoniacal cadmium chlorid solution was used, except in the case of the test tubes where ten cc. was added to each tube. The volumes varied from 30 to 150 cc.

The solution was made by dissolving twenty grams of pure chlorid in 500 cc. of water and adding 500 cc. of ammonia (sp. gr. 0.90).

Five cc. of solution were next employed and made up with water as above to volumes varying from 30 to 100 cc., and depth, one to one and one-half inches, with iodin required, 8.9, 9.1, and 8.7 cc.

One cc. of solution was next taken in varying depth from one and three-fourth to two and one-fourth inches and volumes 60 to 100 cc., with iodin consumed, 8.6, 8.9, and 9 cc.

In these last three experiments, ten to fifteen cc. strong ammonia were contained in each volume as a guard against sufficient acid coming over to dissolve the cadmium sulfid.

Five grams of metal contain 0.0034 gram of sulfur. The reaction taking place is $CdCl_2 + H_2S = H_2S = CdS + 2HCl$; therefore, $32 : 183 :: 0.0034 : 0.01945 =$ weight of cadmium chlorid required to absorb 0.0034 gram sulfur; but one cc. of our cadmium chlorid solution contains 0.02 gram of the chlorid and absorbed all the sulfur, which is practically the theoretical amount to satisfy it. This seemed to us astonishing. We then weighed four 0.01 gram portions of the purest chlorid obtainable (one-half the theoretical amount required). These were diluted to depths of about two inches, with volumes 90 to 100 cc., ten cc. of strong ammonia being used in each case. 7.8, 8.2, 8.1, and 7.7 cc. were the amounts of iodin solution required. According to the theory only about 4.3 to 4.5 cc. should have been used.

To account for this seeming discrepancy several experiments were performed, in each of which fifty cc. (one-third strong ammonia, and the rest water) was used as the absorbent; the iodin required in every case was between five and six cc., showing that ammonia held a large amount of hydrogen sulfid in a form

capable of liberation and titration, but held it with little uniformity and stability.

It would thus seem that 0.01 gram of chlorid with the ammonia added should have retained all the sulfur from five grams of the iron, but, as is evident from the above, it retained only about ninety per cent. of that otherwise held.

This limit of cadmium and its relation to ammonia in absorption is a point we hope to investigate more completely.

The volume seems a question of little importance as shown by the foregoing. Varying depths with the same volume were obtained by using different beakers.

The chlorid seems to be the cadmium salt best adapted for this use since it contains a larger percentage of the metal than the sulfate, nitrate, or acetate. It is evident from these experiments that two to three cc. of our solution diluted to a depth of two inches in a narrow beaker would be a safe absorbent for the sulfur from five grams of any marketable Bessemer iron.

ON THE INFLUENCE OF ALUMED BAKING POWDER
ON PEPTIC DIGESTION, WITH REMARKS
ON A RECENT PROSECUTION.[1]

BY OTTO HEHNER.

It is well known to the public analysts that in 1880 the Recorder of Cambridge decided that baking powder could not be considered an article of food, and did not, therefore, come within the scope of the Sale of Food and Drugs Act, and that, even if it did, the presence of alum in baking powder did not render it injurious to health. In consequence of this decision, alumed baking powder has ever since been freely and extensively sold throughout the country.

All public analysts being agreed to regard alum in bread as an adulteration, and alumed bread having, in consequence, practically disappeared, the decision of the above mentioned Recorder has always appeared to me, as no doubt to most of my colleagues, to be both illogical and absurd, as well as detrimental to the interests of the consumers. Knowing that in the

1 *The Analyst*, November, 1892.

Midlands especially the sale of alumed baking powder was very common, I brought the matter before one of the County Councils for which I act as public analyst, and received their sanction to bring a case into court, in the hope of obtaining a reversal of the Cambridge decision.

Among several samples of baking powder submitted to me for analysis was one which gave the following analytical results :

	Per cent.
Alumina	4.97
Carbonic acid	9.76 and 9.85
Sulfuric acid	15.13
Ammonia	0.12
Starch	33.40
Residue on ignition	31.11

From these figures the composition of the baking powder was calculated to be as follows : 4.97 per cent. of alumina corresponds to 45.80 per cent. of crystallized potash alum, while 15.13 per cent. of sulfuric acid equals 44.58 per cent. alum. The carbonic acid corresponds to 18.63 and 18.80 per cent. of sodium bicarbonate. Subtracting from the ash the anhydrous alum calculated from the amount of crystallized alum (24.96), there is left 6.15 per cent. of soda, equal to 16.66 per cent. of bicarbonate, a figure approximating sufficiently near to the amount calculated from the carbonic acid determination. Thus the entire composition of the powder was :

Crystallized alum	45.80
Bicarbonate of soda	18.71
Starch	33.40
Moisture and not determined	2.08
	100.00

Nearly one-half of the sample consisted, therefore, of alum, while the article upon which the prosecution in 1880 was based contained but twenty-nine per cent. of crystallized alum.

On Feb. 18th, 1880 (*Analyst*, **5**, 67), Mr. West Knights brought a number of experiments before this society, which showed in a marked manner the profound influence of alum in artificial digestions of bread and flour, but inasmuch as I expected that it would be argued, as indeed it was at the hearing of the case, that alum was quite a different thing to alumed

baking powder, and that in the latter the alumina was rendered insoluble by precipitation with sodium bicarbonate, I undertook a number of experiments with alum, as well as with alumed baking powder, to test this matter, and the results of this research I propose now to lay before you.

Theoretically, one equivalent of alum should require for complete precipitation six equivalents of sodium bicarbonate, or 948 parts of alum, 504 parts of sodium bicarbonate. The 18.71 parts of sodium bicarbonate contained in the sample should be able to precipitate 35.19 parts of alum, while 45.80 were actually present. It should be expected, therefore, that when the baking powder in question had been mixed with water, after the completion of the reaction a considerable amount of alumina would be left in solution as alum. I found, however, while there certainly was a marked trace of alumina left in solution, its quantity was less than is required by theory. No doubt the reaction is somewhat more complicated than might at first be expected, not only pure hydrated alumina but also basic alumina salts being precipitated, thus giving the bicarbonate a somewhat greater precipitating power than would correspond to the above proportions. In any case, we have to deal with precipitated alumina hydrate, with basic sulfate of alumina, and with some soluble salt of the base.

According to the directions on the wrapper furnished me, in which the sample had been sold, a heaped teaspoonful of the powder was recommended to be used to every pound of flour. I found the weight of an ordinary teaspoonful to be, on an average of six weighings, 11.21 grams. Assuming that two pounds of flour furnish three pounds of bread, a four-pound loaf of bread made in the manner directed on the wrapper would contain no less than 210 grains of alum.

EXPERIMENTS ON THE DIGESTION OF EGG ALBUMEN.

A solution of pepsin was made, containing 0.02 gram of pepsin in 100 cc. of water. It had previously been ascertained that the pepsin in question was very active and was capable of digesting, under favorable conditions, 2,500 times its weight of hard-boiled white of egg, at 50° C., in about three to four hours.

Five cc. of the pepsin solution contained, therefore, one milligram of pepsin and was able to dissolve 2.5 grams of white of egg in a fluid containing 0.2 per cent. of hydrochloric acid. In a few preliminary blank experiments this was found to be the case, while in the presence of baking powder, in proportion equal to that recommended by the manufacturer, a considerable quantity of albumen could not be brought into solution ; a similar residue was observed when alum itself, to the extent of one-half of the quantity of baking powder, was added in another trial. Quantitative experiments were then made.

Experiment 1.—Two grams of hard-boiled white of egg and 0.05 gram of baking powder were digested with one milligram of pepsin for five hours. The residue left was washed with a little cold water, and the insoluble nitrogen determined by Kjeldahl's process. 0.0407 gram of dry albumen, corresponding to 0.28 of fresh white of egg (with 85.5 per cent. of moisture), or fourteen per cent. of the amount taken, was found insoluble.

Experiment 2.—A precisely similar experiment was made, only instead of baking powder the corresponding amount of crystallized alum (0.025 gram) was taken. Left insoluble 0.0402 dry albumen, or 13.8 per cent. of the amount taken.

Experiments 3 and 4.—In two other similar experiments with the same proportion of baking powder and alum as before, 0.0812 and 0.0743 dry albumen were left, corresponding to 28.0 and 25.6 per cent. of the wet albumen taken.

Experiments 5 and 6.—In these the quantity of baking powder and alum taken was increased fourfold, namely, to 0.2 and 0.1 gram for two grams of white of egg respectively. There were left, after six hours' digestion, 46.7 and 39.2 per cent. of the albumen taken.

Experiment 7.—This was a repeat experiment, with 0.1 gram of alum for two grams of white of egg. After six hours there were left 52.7 per cent. of undigested white of egg.

It is seen that on repetition closely corresponding results could not be obtained, for although the egg had been rubbed through a very fine wire sieve, it was apt to cake together with the formation of little lumps, which could not be easily separated by shaking.

But, speaking generally, the results show that the same quantities of alum, either taken pure or in the form of baking powder, prevent to an equal extent the digestion of hard-boiled white of egg. Parallel with every set of trials a blank experiment was made, without alum or baking powder, and the white of egg was in every case completely dissolved. As far as egg-digestion, therefore, is concerned, alum baking powder is quite as injurious as alum itself.

EXPERIMENTS ON THE DIGESTION OF WHEAT FLOUR.

Wheat flour, containing 1.73 per cent. of nitrogen, corresponding to 10.81 per cent. of albuminoids, was similarly digested. In a blank experiment, without alum or baking powder, there was left undissolved after six hours' digestion of two grams, 0.0280 gram of albumen, or 12.9 per cent. of the albuminoids.

Experiment 8.—In the presence of 0.05 gram of baking powder, with (nearly) 0.025 gram of alum, there was left undissolved after six hours 0.0318 gram, or 14.9 per cent.

Experiment 9.—When the amount of baking powder added was fourfold, namely 0.2 gram, the same percentage of albuminoids was left undissolved, 0.0318 gram, or 14.9 per cent. remaining.

Experiment 10.—With an amount of alum corresponding to 0.05 gram of baking powder, *viz.*, 0.025 gram alum, there remained after six hours a residue of albuminoid of 0.0743 gram, or 34.4 per cent. of the total amount taken.

Experiment 11.—With the fourfold amount of alum there remained 0.1187 gram, or 54.9 per cent.

In the case of digestion of flour, therefore, alumed baking powder has far less influence than the corresponding amount of alum contained in it. Alum itself has a most injurious influence upon the digestion of flour, while that of alumed baking powder is slight.

EXPERIMENTS WITH BREAD.

Experiment 12.—Two grams of the crumb of bread free from alum were digested as before. The residue left after six hours was kjeldahled and found to contain nitrogen corresponding to 0.0231 gram albuminoids. Unfortunately the per-

centage of nitrogen in the bread itself was not determined ; hence the results in the following experiments can only be judged by comparison, but no great error can be committed if it be assumed that the bread contained 7 per cent. of albuminoids, which is the mean given by Koenig in his vast collection of analytical results. In this case 16.5 per cent. of the total were left undissolved.

Experiment 13.—Two grams of the bread crumb, digested with 0.05 gram baking powder, left 0.0315 gram albuminoids undigested ; or, calling the amount left in the blank 100, there were left 136.3, or 22.5 per cent. of the amount taken.

Experiment 14.—With 0.2 gram of baking powder there remained undissolved 0.0407 gram albuminoids, or 172.6 per cent. in comparison with the blank, or 29.1 per cent. of the original amount taken.

Experiments 15 and 16.—In corresponding experiments with alum only, namely, 0.025 and 0.1 gram, there were left 0.0315 and 0.0516 gram. The figures correspond respectively to 136.3 and 223.4, compared with the blank, or to 22.5 and 36.9 per cent. of the total albumen taken.

Curiously, therefore, the influence of baking powder containing alum upon the digestion of bread is more marked than in the case of the raw flour. With small amounts, or rather the amount of baking powder recommended to be taken by the manufacturer, the influence of alum and of alumed baking powder is equal, but with larger quantities the alum acts more detrimentally than does the baking powder.

EXPERIMENTS WITH MILK.

Experiment 15.—Five cc. of milk were digested for six hours without the addition of either alum or baking powder. There were left insoluble 0.0465 gram of albuminoids. In this case also the total amount of albuminoid in the milk had not been estimated, but taking 3.66 to be the average of albuminoids in genuine milk, there was left 63.5 per cent. of the total nitrogenous matter taken.

Experiment 16.—Five cc. of the same milk, digested with 0.05 gram of baking powder, left 0.0681 gram of albuminoids,

or, calling the amount left in the blank experiment 100, there remained 146.5, or ninety-three per cent. of the amount of albuminoids taken.

Experiment 17.—Adding the fourfold quantity of alumed baking powder, there were obtained exactly similar figures, namely, 0.0681 gram, or 146.5 compared with the blank, or 93.0 per cent. of the total taken.

Experiments 18 and 19.—Using the corresponding amount of crystallized alum, namely, 0.025 and 0.1 gram, there were left in each case 0.0562 gram of nitrogenous matter undigested, or, compared with the blank as 100 to 121 parts, or 76.7 per cent. of the amount taken.

It is remarkable that in the digestion of milk the alumed baking powder exerts a more injurious influence than does the amount of alum contained in it, and the smaller amount of alum, whether taken as baking powder or as crystallized alum, acts as markedly as does the four times larger quantity.

Experiments 20, 21, and 22.—In order to ascertain whether baking powder free from alum had any retarding influence upon digestion, three trials were made : A blank digestion of hard-boiled white of egg, without baking powder; a similar experiment with the addition of 0.05 gram of alum-free baking powder, and a third with 0.2 gram of the same baking powder. In all three cases the whole of the white of egg dissolved in five hours, nothing insoluble being left.

It is evident that in the digestion of egg, at least, alum-free baking powder is without detrimental influence.

PHYSIOLOGICAL EXPERIMENTS.

I weighed out four quantities of alum baking powder, amounting to two grams. This is very nearly the quantity which would be contained in four ounces of bread, if made according to the direction on the label (the exact amount would be 1.88 grams), mixed them with water, waiting until the effervescence had finished, added some sugar to render the dose palatable, and took one dose myself, giving the other three to my assistants. I requested them to let me know next morning their symptoms, without previous communication with each other.

We were all in perfect health before taking the dose. Already, about an hour-and-a-half afterwards, unpleasant symptoms began to appear. Speaking for myself, I experienced first a feeling of great weight in the origin of the stomach, later on pains in the epigastric region, slight difficulty in breathing, headache, and ultimately slight diarrhœa,—symptoms resembling an attack of indigestion. My assistants were similarly affected, and felt discomfort for several days.

After complete recovery, I took in a similar manner one gram of the powder, or a quantity which would be contained in as little as two ounces of bread. Similar symptoms, almost to an equal degree, manifested themselves.

I have, therefore, come to the following conclusion : That alumed baking powder exerts a most injurious influence upon digestion, whether artificial or within the body ; that the presence of alum in baking powder must be regarded as an adulteration injurious to health ; that samples containing alum should be condemned as injurious, even though magistrates and recorders declare alum to be quite harmless ; and that the sodium bicarbonate contained in the baking powder does not neutralize the objectionable qualities of the alum. This, indeed, was not to be expected upon chemical grounds, inasmuch as the precipitated hydrate of alumina is readily soluble in dilute acid, and in the baking of bread the temperature does not rise in the interior of the loaf to anything like the point at which hydrate of alumina loses its water of constitution.

At the hearing of the case in question certain evidence was given for the defence, to which I will shortly refer. Mr. Wynter Blyth, who in his work on " Foods " declared "there can be no difference of opinion that it (alum in bread) is a serious adulteration, and not to be permitted," and who has, in his capacity as public analyst, condemned samples of bread containing alum as adulterated, came forward on behalf of the manufacturers of this baking powder, and stated that he considered alum in bread to be an entirely different thing to alum in baking powder ; and that he had for some time past used in his household bread made with the baking powder in question without experiencing any injurious effects. Mr. F. Sutton, public analyst, who, as far

back as 1872, had given a testimonial to the identical maker of this baking powder, in which it was lauded in the strongest language, went further, and attributed to alumed baking powder the valuable property of fattening pigs, if added to their ordinary food. He would continue to condemn alum in bread, but would not object to alumed baking powder. Dr. Thudichum, who, not being a public analyst, felt himself still freer from restraint, strongly stated that he considered alum itself to be possessed of valuable digestive properties. No attempt was made on the part of these three gentlemen to rebut the digestion experiments which I laid before the Bench, as I now lay them before you to-night, only the general statement being made that natural gastric juice was an altogether different thing from the artificially prepared article ; and that as to my personal feelings and those of my assistants, all that could be urged was that we must have persuaded ourselves we were ill when all the time in reality we were perfectly well.

The magistrates, in view of this conflict of evidence, which certainly was quite unreconcilable, dismissed the case upon the same grounds as those enunciated by the Recorder of Cambridge.

I trust that my present contribution to the subject will go some way towards advancing the matter to a final and more satisfactory settlement. It is clearly my opinion that as public analysts we should be acting contrary to public interests if we passed alumed baking powder as a genuine and legitimate article.

My best thanks are due to my assistant, Mr. W. P. Skertchly, for carrying out the analytical work involved in this investigation.

DISCUSSION.

The Chairman, in inviting discussion, said he felt sure that the members present had all listened with much interest to the paper just read. Mr. Hehner had gone into the experimental side of the question very fully, and he (the chairman) thought that the strong evidence as to the deleterious action of alumina on the human economy which had been brought before them that evening, could not fail to convince any unbiased mind that its presence in baking powder was highly undesirable.

Mr. Cassal thought it desirable that by some expression of opinion on the part of the members of the Society the president should be supported in his position in the baking powder case under notice, of which, of course, they had all heard. It was extremely unfortunate that prominent public analysts should appear in Court and should give evidence against one another—especially evidence of the kind they had heard about, and he was exceedingly surprised at the statements which Mr. Wynter Blyth and Dr. Thudichum made in the case. It was equally regrettable that Mr. Sutton, who was a well-known public analyst, should have given the evidence that he was reported to have given. He (Mr. Cassal) gathered from what the president had said that hydrate of alumina was to be regarded as, in a sense, equally injurious with alum, and as, in fact, *the* injurious substance which might be present in bread that had been made from alumed baking powder. The contention of Messrs. Blyth and Sutton appeared to be that alum, as alum, was the only thing that could be injurious in bread or flour. It was very important that the president's experiments should be made known, as far as possible, among public analysts, inasmuch as they appear to show that hydrate of alumina was in itself a distinctly injurious substance. That at once disposed of the only argument that Messrs. Blyth and Sutton had, namely, that carbonate of soda having precipitated hydrate of alumina, alum could no longer be present as such, and, therefore, that there could be no injury to the health of the consumer. It must be plain to the society that if the magistrates had properly appreciated the weight of the evidence before them, they ought to have given their decision in favor of the County Council. It was plain enough that they had definite scientific experiments on the one side, and mere assertions, of little or no scientific value, on the other. He therefore felt that the meeting would be perfectly justified in supporting the president of the Society, and in expressing their regret that two prominent public analysts—and two prominent members of the Society—should have given the evidence that they had given on that occasion.

Mr. H. Droop Richmond said it appeared to him that the president's experiments were hardly as conclusive as might have

been wished. For instance, the experiments which he had made, and in which he and his assistants had swallowed alumed baking powder, were not, to his mind, conclusive. When given in that form it was concentrated, but if the quantity were put into bread, it was spread over a much larger surface, and consequently only a small quantity of the alum was exposed to the action of the pepsin in the stomach. He believed that if the experiments were repeated, and if the president and his three assistants ate four ounces of bread containing the baking powder, the experiments would be more conclusive. He thought that in the case of bread, the peptic digestion only played a small part in the total digestion. Pepsin had no amylolytic function, and the starchy portion would protect the remainder from attack during the short time it remained in the stomach ; he believed that the pancreatic digestion played the more important part. He hoped that if the president were going to make any more experiments, he would try them with pancreatic extract, and see if there was the same retarding effect there. He did not wish to be inferred, in suggesting to the president that he should make other experiments, that the experiments already carried out were not worth anything, because he thought they were extremely valuable, but he did not think they had gone as far as they could have been pushed.

The president felt bound to say, in reply to Mr. Richmond's remarks, that he thought, given plenty of gastric or pancreatic juice, the food might have been digested in spite of the alum. Probably individuals in very good health, and blessed with excellent digestions, might be able to digest bread even if it contained alum. What he did wish to lay particular stress upon was, that an article which, when taken in a moderate quantity and diluted with water, was injurious, should not be used in food. Of course, the injurious effects might be minimized in the case of a healthy person.

Mr. Cassal asked whether the case was appealed against, or whether there was any question of appealing ? He supposed the usual excuse was made that a decision had been given on a question of fact and not of law.

The president replied that the County Council came to the

conclusion that it was no use appealing, since evidence similar to that given at Ilkeston would certainly be brought forward again ; and in view of a direct conflict of evidence an appeal would probably fail.

Mr. Cassal pointed out that the decision of the Recorder of Cambridge, or the decision of a magistrate, did not make law, and had really no weight at all ; and he would take the opportunity of suggesting that whenever possible these gentlemen should be set right as far as was practicable. He thought it a very excellent thing to do in the interests of the public. Moreover, the very unfortunate circumstances which the president deplored were only brought out on occasions of that kind, and they could hardly hope for the reforms required, unless the evil was clearly before the members of the profession.

The president wished to add that the case referred to was not finally decided and could be taken up again at any time. He had brought these experiments forward in order gradually to accumulate matter for such a contingency.

IMPROVEMENTS IN REINSCH'S PROCESS.[1]

By John Clark, Ph.D.

Reinsch's process as carried out in the ordinary way, is capable of demonstrating the presence of very minute quantities of arsenic, and, according to Letheby, it withdraws every, and the smallest, trace of arsenic from organic mixtures, but there are two objections to its use in medico-legal cases.

1st. When the quantity of arsenic is small, a stain is obtained which it is sometimes difficult to identify as arsenic, because the coated copper when heated is apt to give a layer of chlorid of copper and organic matter, instead of arsenious acid; and

2nd. It is not suitable for the quantitative estimation of arsenic, as it is not possible by means of heat to volatilize the whole of the arsenic from the copper.

The author's improvements consist in identifying the arsenic or antimony on the copper with greater certainty, and at the same time estimating the amount of each when they occur together.

[1] From the *Proceedings* of the London Chemical Society, May 18, 1893.

For this purpose he digests the coated copper in a cold mixture of dilute caustic potash and peroxid of hydrogen, which dissolves the arsenic and antimony, and converts them into arsenate and antimonate of potassium. The solution is then boiled, filtered to get rid of the oxid of copper, evaporated to small bulk, and distilled with ferrous chlorid and strong hydrochloric acid. The distillate is then saturated with hydrogen sulfid, and the arsenic weighed as sulfid, after being freed from traces of sulfur by washing with carbon bisulfid and alcohol. The residual liquid, from which the arsenic has been thus removed by distillation, is then tested for antimony.

<div align="center">DISCUSSION.</div>

Dr. Bernard Dyer drew attention to a remarkable difference in the results obtained on testing for arsenic by Marsh's process when the zinc used was in the shape of rods instead of being granulated. Some time since he had detected arsenic, not a mere trace, but a tangible, weighable quantity, in a certain pigment, but his results were disputed by the maker of the color, who stated that a test made with rigid precautions by another operator had afforded no evidence of the presence of arsenic. The speaker had therefore met the other operator, and the following very curious results were obtained : An ounce or two of his (Dr. Dyer's) highly purified granulated zinc was introduced into the Marsh apparatus, together with pure hydrochloric acid ; at the end of an hour no appreciable deposit was formed in the heated tube, but on introducing two grams of the pigment a dense arsenical mirror was soon obtained. The apparatus was then washed out, and charged with cast rod zinc, brought by the challenging operator ; not only, however, was no deposit formed in the tube during the blank trial, but also on introducing two grams of the pigment no indication of the presence of arsenic was obtained, although the experiment was continued during an hour. Further experiments were made with this cast zinc, in which arsenious acid was deliberately added ; when small fractions of a milligram were taken, and gas was slowly evolved, the arsenic was almost completely held back, and was but very partially deposited even when several milligrams were

taken, the results being altogether different from those obtained on using the granulated zinc. A number of samples of cast zinc were found to behave similarly. He had no doubt that some condition, probably of a physical kind, prevailed in cast zinc that did not prevail in the case of granulated zinc. The matter required further investigation, as it was one of obvious importance in toxicological work. There was little doubt that the arsenic is precipitated in the generating bottle. Even granulated zinc produces some precipitation. It has been already shown that the frequently advocated use of platinum in the generating bottle tends to hold back arsenic, and it seems probable that some couple may be formed in cast zinc.

PATENTS OF INTEREST TO CHEMISTS.

EDITED BY A. H. WELLES.

"Sublimed lead pigments" are prepared by E. O. Bartlett by driving off lead fumes from lead bearing material in suitable furnaces, carrying the fumes through flues at a red heat, and separating the purified fumes by screening from the gaseous products (496,038). Two more patent processes for the manufacture of white lead. 496,109, A. B. Browne, patentee, consists in placing lead in a solution of a nitrate of an alkaline base; the current is then passed and the alkaline hydrate formed at one pole precipitates the lead which has been dissolved, and the resultant lead hydrate is dried in an atmosphere of carbon dioxid. 495,490 is the invention of Andrew Honman and Victor Vulliez. Lead sulfate is dissolved in a solution of caustic soda or potash or ammonium acetate, heated, and precipitated with an alkaline carbonate and dried.

Ludwig Rissmüller manufactures superphosphates from kettle residues of glue factories by mixing residues with warm sulfuric acid (50° B.) and heating to 200° F. After the nitrogenous matters are dissolved by the acid, the gypsum is precipitated and the fat rises to the surface, the separated solution is treated with phosphate of lime to take up all the sulfuric acid (494,939). 494,940 is a similar process, applied to animal carcasses, etc. Omar T. Joslin treats tank water with sulfuric acid, adds five to thirteen per cent.

of a concentrated solution of waste fullers' earth dissolved in sulfuric acid, and dries the product at 300°–350° F. (495,042); and 495,043 is also his patent for manufacturing fertilizer from tank water in which acid phosphate of calcium in combination with fullers' earth is used, instead of the latter alone.

H. L. Castner manufactures the higher oxids of sodium and potassium from the alkali metals by heating to 300° and oxidizing the metals by the action of air with a decreasing proportion of nitrogen (494,757). James J. Fronheiser mixes an aqueous solution of iron sulfate and sulfuric acid, evaporates, and adds finely, divided ferruginous matter and heats in his process for pigments (495,197).

495,028 covers a process for tanning leather, granted Martin Dennis. After treatment in a bath of basic chlorid of chromium to fix the gelatin, the hides are subjected to a bath of suspended carbonate of calcium. Heinrich Thies and Emil Herzig dip articles to be bleached first in hydrofluoric acid solution then steam and wash in a bath containing an alkaline earth compound, again steam and treat with boiling caustic alkali lye (496,072). To preserve meat, F. G. Dosmond and Jean F. Rozès exhaust air from the receptacle, and introduce under pressure gases obtained by calcining charcoal which has absorbed water (496,047), Peter Murray uses the following scheme to preserve timber: After coating with coal oil or mineral oil, animal fat, and brimstone, he burns the composition while applied to the timber until the composition is consumed (495,991). Samuel P. Sadtler and John H. Grimm patent a process for obtaining licorice extract (495,271) and Alfred Dervaux purifies water by charging an upwardly flowing column with lime at a point below the outlet of the water, forcing the lime to gravitate against the water and decanting the charged water at a safe distance below (495,313).

Peter T. Austen obtains a solid extract of sumac, hemlock, etc., by incorporating an alkaline nitrite (495,768). Fritz Bender patents a blue dye derived from dimethyl metamido-cresol and derivatives of aromatic amines (494,838) and R. E. Schmidt and Paul Tust obtain an alizarin dye by oxidizing beta nitro-anthropurpurine with manganese dioxid in sulfuric acid solution (496,139).

Eugen Langen has a patent process for refining sugar (495, 614), and Dr. Fahlberg takes out two patents on his improved process for manufacturing pure saccharin, 496,112 and 496,113. A dry mixture of para sulfaminbenzoic acid and ortho sulfaminbenzoic acid is added to an aqueous solution of an alkali or alkaline earth containing just enough alkali to neutralize and dissolve only the ortho acid, filtering off the liquid from the undissolved para acid, and adding to the filtrate an acid stronger than the ortho sulfaminbenzoic acid, whereby the saccharin is precipitated. Wm. W. Jacques uses grains of carbon treated with alumina for granulated material for transmitting telephones (495,090). Jonas E. Blomén dissolves picric acid and a hydrocarbon separately, then mixes, and the "picrated" hydrocarbon is dissolved in nitroglycerol, forming a blasting compound (495, 178). Robert Hutchinson has a composition for a lubricant, lime combined with fatty acids in excess, with a mineral or hydrocarbon oil and an alkali "pinate" (496,225). Paper pulp, sour milk, albumen, lime, and chlorid of zinc form the combination which Wm. P. Emery proposes to use for making railroad ties (495,581). To make coal-briquettes, John N. Macrath adds to coal-dust a binder of a viscous liquid (made by boiling wood moss in silicic acid) and a solution of silicic acid (495,679). R. J. Parke and Isaac Goodman have a paint-filling composition (496,277) and "soap, ether, ammonia, glycerol, alcohol, and water" form a cleaning compound patented by Charlotte E. Moor (496,274). Otto Jensen and R. Keck claim the rock "phonolite," sodium sulfate, and limestone as a glass composition (494,636).

Another patent wall-plaster, Barbara Dirnberger the inventor, consisting of sand, plaster of Paris, slaked lime, muriatic acid, lime, soluble glass, glue water, and tissues of fiber (494,981).

Frank S. Culver has two patents on a fire-proofing composition, 495,149 and 495,166, the former containing a large proportion of asbestos fiber, plaster of Paris, and a small proportion of gypsum cement with a binding fiber of jute or hemp, while the latter patent omits the gypsum. Herman Giessler mentions pulverized magnetic oxid of iron, a metallic soap, a glass flux, and a refractory body-substance as emery or metallic powder,

as a compound for coating metallic surfaces with a film of vitreous luster and dark violet blue color (495,629). A compound of cresol—para-isobutyl-ortho-cresol iodid—a yellow powder, soluble in ether, chloroform, and olive oil, which decomposes above 60° C., and on further heating gives off iodin vapors, is patented by Josef Messinger and G. Vortmann (495,204).

Thomas A. Edison has a roller for crushing ores (498,385). N. L. Raber (497,603) and A. B. Kittson (497,669) have each an amalgamator, and Uriah Cummings patents his ore crusher (498,424). C. B. Walker has a new form of ore-concentrator (497,843), and Charles G. Brown a patent ore tank for leaching (497,856). Orrin B. Peck protects his centrifugal ore separator by 497,204, while F. H. Wheelan (498,597), W. P. Miller (497,474), Charles G. Buchanan (497,117), and Albert M. Bair (496,391) have each a separator. William Stubblebine's metallurgical furnace (498,089) and M. Mannaberg's steel-smelting furnace (498,670) are recent issues, as well as Joseph McClelland's tuyere (498,565). An apparatus for removing matte from slag is the joint invention of Thomas Drohan and Thomas Pearce (496,823).

F. W. Cleghorn separates precious metals from their ores by filtering through the ores a solution of sulfuric acid and sodium chlorid, placing metallic iron in the filtrate and passing the current (497,014), while Henry Parkes uses one of two methods to accomplish the same end, treating the ores with potassium cyanid in the presence of oxygen under pressure (496,950), or treating with chlorin and then agitating with oxygen under pressure (496,951). To concentrate and separate ores, John W. Meier heats and converts into ferric oxid, then into magnetic oxid by heating with carbonaceous substance, and reducing gases as carbon dioxid and then separates with the magnet (497,804).

Martin Wanner proposes to manufacture carbon disulfid from reduced sulfid ores by mixing the finely divided reduced sulfid with powdered carbon, then moistening the mass with liquid hydrocarbon, heating in a closed retort, condensing the carbon disulfid, and removing reduced metal from furnace (497,256). W. R. Ingalls and Francis Wyatt treat complex ores as follows:

First, roast, to convert into sulfates, recovering sulfur driven off as sulfuric acid; next, lixiviating with water and said sulfuric acid, removing iron if necessary, precipitating zinc as carbonate or basic carbonate, using sodium carbonate, and burning to zinc oxid, evaporating sodium sulfate and heating with sodium chlorid and coal to convert into sodium sulfid, then into bicarbonate of soda by dissolving in water and precipitating with carbon dioxid and heating the precipitate to convert into sodium carbonate (497,473). C. W. Beehler is the inventor of a hydrothermal mining process (497,513), which consists in filling a closed casing with a liquid body, inserting in bore hole, and heating by electric resistance coil, so that the expansive force of the liquid may be exerted within the drill hole. Louis Aronson (497,621) for an electro-tinning bath uses a combination of water, ammoniacal alum, chlorid of tin, sodium pyrophosphate and caustic soda.

Finely powdered wood charcoal with animal charcoal is a combination given by H. A. Harvey for supercarburizing steel (498,390). John A. Hunter has three patents; 498,061 is a process for increasing per cent. of carbon in low steel by subjecting molten metal in a suitable converter to the action of a blast composed of the gases resulting from heating together hydrochloric acid, calcium chlorid, carbon, and sodium chlorid ; 498,062 is a method for converting iron into steel by heating in a crucible or retort, subjecting to action of a gas containing chlorin, oxygen, and hydrogen, evolved from hydrochloric acid, calcium chlorid, and sodium chlorid; 498,063 is another patent on a process for increasing per cent. of carbon in steel, by subjecting the red hot metal in a crucible or retort to the action of chlorin and oxygen, which have first been brought into contact with heated carbon. T. S. Harrison and C. Semper have two patents ; one (497,570) an "aluminous compound," composed of sulfate of aluminum, and a double sulfate of aluminum and soda; and the other (497,571) an improvement in the process for making same, which consists in hardening or drying by the addition of sulfate of soda.

An apparatus for recovering alkali (497,088) belongs to Henry Blackman, and Thomas Craney claims 496,863, an apparatus

for the electrolysis of salt, and 496,866, an arrangement for washing salt, M. M. Monsanto has an improved process for manufacturing salt (496,615). Philip C. Hoffman treats pulverized phosphates of the "Florida phosphate" class with sulfuric acid, heats, and maintains the temperature above the normal temperature occassioned by chemical action, which is usually 50° C., but yet below that at which pyrophosphates are formed (496,687). M. L. Griffin (497,785) precipitates calcium carbonate by adding lime to a soluble carbonate, then mixes the precipitate with clay, drys, calcines, and grinds to form Portland cement.

Alfred Wohl and Alexander Kollrepp (498,000) mix saccharine solutions containing sixty per cent. or more of sugar with dilute acid, heat the mixture and neutralize the acid to obtain invert sugar. Georges de Laire has a process for manufacturing vanilloyl-carbonic acid and vanillin (497,546).

[The specification and drawing of any U. S. Patent in print may be obtained from the publisher of this Journal. Applications must be accompanied in all cases by twenty-five cents for each patent specification wanted. BE CAREFUL TO WRITE THE NUMBER LEGIBLY.]

NEW BOOKS.

THE ELEMENTS OF QUALITATIVE ANALYSIS. BY WM. A. NOYES, PH.D., PROFESSOR OF CHEMISTRY IN THE ROSE POLYTECHNIC INSTITUTE. 3d edition, revised. New York: Henry Holt & Co., 1893, 97 pp.

This book has evidently been written by one who understands the needs of the student in qualitative analysis. The descriptions are clear and concise, and ready reference to the text is facilitated by the heavy head lines which mark the different paragraphs. There are valuable "tables of reactions" for the bases and acids, which the author credits to Dr. Biedermann's "Chemiker Kalender," and an important supplement to this edition is the "special part," which gives direction for the qualitative examination of potable waters, of iron and steel, and of gold and silver ores. The directions in the appendix for making the ordinary reagent solutions are also a noteworthy feature of the work. A. H. W.

NOTES ON THE HIGHER OXIDS OF NICKEL.

BY E. D. CAMPBELL AND P. F. TROWBRIDGE.

MANY attempts have been made to obtain a satisfactory volumetric method for the determination of nickel based on its oxidation by means of bromin, chlorin, sodium hypochlorite, or hydrogen peroxid in the presence of an alkali hydrate or carbonate.

The degree of oxidation has been determined by means of the amount of iodin liberated from hydriodic acid or the amount of ferrous salt oxidized to ferric salt. Any method based on this principle must assume constant degree of oxidation of nickel under given conditions; and chemists do not agree in their statements in regard to the composition of the oxid obtained.

Fleischer in his volumetric analysis (translated by Muir, p. 77, and in *J. Chem. Soc.*, **38**, 287, also in *J. prakt. Chem.*, **2**, 48), gives the following method as devised by himself: Nickel and cobalt are both oxidized to nickelic oxid, Ni_2O_3, and cobaltic oxid, Co_2O_3, by bromin or sodium hypochlorite in a solution made alkaline by sodium hydroxid. The solution is heated until the precipitate turns a deep black. After filtering and washing the precipitate is reduced by hydriodic acid or ferrous salt and the liberated iodin titrated by standard sodium thiosulfate or the excess of ferrous salt by potassium bichromate. Another sample is oxidized in the same way. The precipitate is treated with ammonium hydroxid which reduces the nickel, and then the cobalt is estimated by reduction with hydriodic

acid.   He assumes the constancy of the nickelic and cobaltic oxids, Ni_2O_3, Co_2O_3, and claims very accurate results from this method.

Donath, in *Berichte*, **12**, and in *J. Chem. Soc.*, **38**, 287, assumes the composition of the oxidized nickel to be Ni_3O_4 and bases his method on this..   Carnot, in *Compt. rend.*, abstracted in *Chem. News*, **59**, 183, states that the composition of the precipitate obtained by the action of bromin or sodium hypochlorite on a solution of nickel, made alkaline by a fixed alkali hydrate, is exactly Ni_2O_3.

On the other hand Bayley (*Chem. News*, **39**, 81) has shown the instability of nickelic oxid, and that, by the action of sodium hypochlorite on a solution of nickelous nitrate, made alkaline by sodium hydroxid, a precipitate corresponding to Ni_2O_3 is obtained.   The precipitate is partially reduced upon boiling the solution in which the nickel is precipitated.   His method of determining the degree of oxidation was to boil the solution in which the precipitation was made for a few minutes only, in order to decompose the excess of sodium hypochlorite.   Then add potassium iodid to the solution containing the precipitate, and after acidifying with hydrochloric acid, titrate the iodin liberated with sodium thiosulfate.   He also finds in precipitating the cobalt in the same manner an oxid, Co_3O_4, similar to that obtained from the nickel, but more stable.

McCulloch (*Chem. News*, **59**, 205) essentially substantiates Bayley's work and in the same journal (**56**, 27) states that the precipitate obtained by the action of bromin and sodium hydroxid on a boiling solution of nickel varies from Ni_4O_7 to Ni_2O_4.

Constantin Krauss (*Chem. News*, **63**, 255) claims that the oxid of nickel obtained by the action of bromin or sodium hypochlorite upon a solution of nickel made alkaline by potassium hydroxid is of a lower degree of oxidation than Ni_2O_3.

Experiments were made at the laboratory of the University of Michigan to see if, in any way, this higher oxid of nickel could be obtained constant enough for quantitative work.   Failing in this, an attempt was made to push the degree of oxidation as high as possible and to investigate the stability of the precipitated oxid.

The solution of nickel used in the experiments was a neutral solution of nickel sulfate (four liters of solution were made from chemically pure nickel sulfate) showing by electrolysis 0.00467 gram of nickel per cc. Samples of twenty cc. each of this solution were taken (0.0934 gram of nickel) for oxidation. These samples were diluted to 150 cc., then oxidized with bromin and sodium carbonate under varying conditions; the precipitate filtered and washed thoroughly with hot water and subsequently reduced with hydriodic acid, and the liberated iodin determined with standard sodium thiosulfate.

The method of titration was as follows: 300 cc. of water were run into a large Florence flask; to this were added six grams of potassium iodid and two cc. of hydrochloric acid (sp. gr. 1.21). The filter containing the washed precipitate was pushed into the flask, which was then tightly stoppered, and the contents thoroughly shaken until the filter was completely disintegrated and the precipitate dissolved. The precipitate dissolves readily, but unless the filter paper is broken up thoroughly, the end reaction is not quite as sharp. After shaking, the cork and neck of the flask are carefully rinsed with water, and standard sodium thiosulfate run in until the iodin is nearly all reduced. Two cc. of starch solution are then added and the titration completed. With these precautions the titration is accurate to one drop of decinormal sodium thiosulfate.

The experiments first made were to find the best method of oxidation, both as to degree of oxidation of the nickel and ease and rapidity of the filtration and washing of the precipitate.

From the equation $Ni_2O_3 + 2HI + 4HCl = 2NiCl_2 + I_2 + 3H_2O$, 0.0934 gram of nickel would liberate 0.2016 gram of iodin; and, since all of our work has been done with the same amount of nickel, an examination of the amounts of iodin liberated under different conditions will be the easiest way of determining the degree of oxidation.

First.—A cold mixture of a saturated solution of sodium carbonate and bromin was added to cold nickel sulfate solution (twenty cc. of nickel sulfate solution diluted to 150 cc.). The green precipitate of nickelous carbonate was formed with no black precipitate to indicate oxidation.

Second.—The cold mixture of bromin and sodium carbonate was added to a hot solution of nickel sulfate. The black flocculent precipitate obtained was very difficult to filter and wash, and liberated 0.0316 gram of iodin.

Third.—The mixture of bromin and sodium carbonate was then heated until the bromin all passed into solution, giving a pale yellow color to the mixture. This was added to a cold solution of nickel sulfate with no black precipitate to indicate oxidation.

Fourth.—This hot mixture of bromin and sodium carbonate was also added to a hot solution of the nickel with very slight oxidation, showing the bromin to have combined with the sodium carbonate in such a way as to make it unavailable for the oxidation of nickel.

Fifth.—Experiments were then made by adding sodium carbonate to the nickel solution, then bromin, and heating. The black precipitate obtained was difficult to wash and liberated 0.1935 gram of iodin.

Experiments were continued, varying the degree of heat both of the nickel solution and of the sodium carbonate solution; also, by adding the bromin before heating, or adding sodium carbonate, and by adding the bromin after adding the sodium carbonate. These experiments led to the following method : Add an excess of bromin to the cold nickel solution. Gradually bring this to the boiling point, stirring occasionally, and when all free bromin from the bottom of the beaker is in solution, add to the boiling nickel solution a boiling saturated solution of sodium carbonate in slight excess. The precipitate obtained in this way filters and washes with hot water very readily, and on reduction and titration shows a higher degree of oxidation than that obtained by any of the previous methods. Consequently this method was the one used in the following experiments, and the results show the degree of oxidation and stability of the precipitate obtained.

Six samples, oxidized, filtered, and washed side by side and titrated successively, all within two hours of oxidation, showed the degree of oxidation secured by the amount of iodin liberated to have been as follows :

No. of sample.	Weight of Ni taken.	Weight of iodin liberated.	Iodin calculated for Ni_3O_3.
1	0.0934 gram	0.2403 gram	0.2016
2	0.0934 "	0.2264 "	0.2016
3	0.0934 "	0.2150 "	0.2016
4	0.0934 "	0.2061 "	0.2016
5	0.0934 "	0.2020 "	0.2016
6	0.0934 "	0.1920 "	0.2016

Seeing from the above results that time played an important part in the reduction of the nickel, many experiments were made in which a close account of time elapsing from oxidation to titration was kept. It was found that filtration and complete washing could not be accomplished in less than fifteen minutes from the time sodium carbonate was added, even when filtration was begun in less than three minutes from the time sodium carbonate was added. The completeness of the washing was indicated by the failure to get a precipitate with silver nitrate in the washings.

A sample was allowed to stand one week in the beaker after oxidation, filtered cold, but washed with hot water. Titration immediately after washing showed 0.1141 gram of iodin to have been liberated.

A sample filtered and washed immediately after oxidation, but allowed to stand one week at temperature of laboratory upon the filter, liberated 0.1669 gram of iodin. This shows a degree of oxidation not far from Ni_4O_7, which would liberate 0.1612 gram of iodin. Ni_6O_{11} (Bayley) would liberate 0.1512 gram of iodin.

Two samples were allowed to stand two hours on the hot plate at the boiling point after oxidation. They were then filtered and washed rapidly. Upon reduction they liberated respectively 0.1897 gram and 0.1948 gram of iodin, less than Ni_3O_3. Another sample was filtered and washed rapidly, but allowed to stand on the filter one hour before titration. This liberated 0.2128 gram of iodin, showing greater oxidation than Ni_3O_3.

The following table of selected experiments will show the amount of iodin liberated when the time from the addition of sodium carbonate to the introduction of the precipitate into the titrating flask did not in any case exceed twenty minutes:

Weight of Ni taken.	Weight of I liberated.	Calculated formulas.
0.0934 gram	0.2036 gram	0.2016 gram = Ni_2O_3
0.0934 "	0.2067 "	....
0.0934 "	0.2087 "	....
0.0934 "	0.2151 "	....
0.0934 "	0.2264 "	....
0.0934 "	0.2289 "	0.2294 gram = $Ni_{12}O_{19}$
0.0934 "	0.2390 "	....
0.0934 "	0.2425 "	0.2419 gram = Ni_5O_8
0.0934 "	0.2616 "	....
0.0934 "	0.2704 "	0.2688 gram = Ni_3O_5

These results show how greatly the oxidation of the nickel may vary even under similar conditions. Not more than ten or fifteen results were obtained that liberated more than 0.240 gram of iodin, while the great majority of the experiments gave from 0.210 gram to 0.235 gram of iodin. The last result shows the highest degree of oxidation that could be obtained in this manner.

Knowing that the presence of a non-oxidizable dyad metal greatly facilitates the oxidation of manganese, a similar method was employed with nickel. From 0.050 gram to 0.075 gram of magnesium oxid in the form of magnesium sulfate were added to the 0.0934 gram of nickel and the method of oxidation proceeded with the same as before. When the time of filtration and washing was kept within twenty minutes the following results were obtained:

Weight of Ni taken.	Weight of I liberated.	Calculated formulas.
0.0934 gram	0.2891 gram	0.2688 gram = Ni_3O_5
0.0934 "	0.2941 "	0.3018 gram = Ni_4O_7

Blanks containing 0.050 gram of magnesium oxid in the form of magnesium sulfate, but no nickel, were diluted to 150 cc. After adding bromin in excess the solution was gradually brought to the boiling point. To this the solution of boiling sodium carbonate was added. The precipitate of magnesium carbonate was filtered and washed and upon titration showed no oxidation.

From the experiments made, we may justly conclude that the higher oxids of nickel are unstable compounds, and that an oxid higher than Ni_3O_4 can quite readily be obtained. That the oxid NiO_2 exists is doubtful, as that would require that

0.0934 gram of nickel should liberate 0.4029 gram of iodin or 0.1088 gram more than at present secured.

CHEMICAL LABORATORY
OF THE UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.
May 27, 1893.

A RECENT POISON CASE.

BY WILLIAM P. MASON.

A number of interesting points, bearing upon the chemico-legal side of arsenical poisoning, having arisen during a recent trial with which the writer was connected as expert, the following is given as a brief report 'of the case.

The deceased, a farmer, bachelor, sixty-five years of age, and in good health, was taken violently sick shortly after breakfast, with vomiting and distress in the stomach. Although a physician was summoned, the symptoms increased in severity, and a little after midnight death ensued. The funeral took place three days later. Certain very damaging pieces of circumstantial evidence having been collected, the housekeeper was arrested on the charge of murder, it having been shown among other things, that on the day preceding the death she had purchased an ounce of white arsenic.

Thirty-five days after death (from March 20 to April 25), the body was exhumed, and found in a state of remarkable preservation, and free from cadaveric smell. The stomach presented evidences of inflammation.

Those portions sent to this laboratory for examination were the stomach, portion of intestine, portion of liver, one kidney, and the heart. Arsenic was found in all these parts. White octahedral crystals were found in the contents of the stomach, which on separation gave arsenical reaction.

The methods of testing for the arsenic found in the various tissues were the Marsh and Reinsch, with the usual precautions, checks, and modifications.

The arsenic as found was :

	Gram.
Stomach and intestine	0.2376
Liver and kidney	0.0032
Heart	0.0007
Total as metallic arsenic	0.2415

This would correspond to 4.91 grains of white arsenic.

These weighings having been of tube deposits of metallic arsenic derived from the Marsh test, they did not represent all the arsenic present in the tissue, there having been unavoidable loss. Allowance having been made for such loss, the estimated amount of white arsenic present was six grains.

The amount of arsenic recovered and produced in court was, however, in quantity sufficient to produce death. Some time after the analytical report was made to the coroner, it was learned that an embalming fluid, highly arsenical in character, had been used upon the body by the undertaker at the time of preparation for burial. It is important to note that no injection of this embalming fluid was practiced, but that cloths wrung out in the fluid were laid upon the face and chest and were kept constantly wet therewith during a period of many hours. In all about two quarts of embalming fluid were so used. Its composition appeared to be a strongly acidified solution of sodium arsenite and zinc sulfate. Only the arsenic and zinc were determined quantitatively, and they were found to be, zinc (metallic) 1.978 per cent. and arsenic (metallic) 1.365 per cent. by weight. An amount of this fluid measuring 15.7 cc. would thus contain a weight of arsenic equal to that actually recovered from the body.

Extended medical testimony was offered by the people tending to show that, under the given circumstances, no fluid of any kind could have reached the stomach through the nose or mouth after death, thus anticipating what the defense afterwards claimed, that the undertaker was responsible for the arsenic discovered in the remains.

In order to gather further light upon the possibility of cadaveric imbibition of embalming fluid through the unbroken skin, test was made for zinc in the heart and stomach, and greatly to my surprise distinct traces of the metal were found in each instance. That at least a portion of the arsenic found in the body was due to post mortem causes was thus distinctly proven. A weighed portion (sixty-two grams) of the stomach and contents was then most carefully analyzed quantitatively for both zinc and arsenic with the following results: Arsenic, 0.0648 gram,

and zinc, 0.0079 gram. Bearing in mind the relative quantities of the two metals in the embalming fluid, it will be seen that the arsenic found in the sixty-two grams of the stomach was nearly twelve times larger than it should have been to have balanced the zinc which was also present. This fact, together with the discovery of crystals of white arsenic in the stomach, constituted the people's case so far as the chemical evidence was concerned.

The defense made an unsuccessful effort to show that the crystals of the tri-oxid originated from the spontaneous evaporation of the embalming fluid. The people met this point by proving that such fluid had been abundantly experimented upon by exposure to a very low temperature during an interval of several months, and also by spontaneous evaporation with a view of testing that very question, and that the results had in every case been negative. Special importance was given these experiments because of the well known separation of octahedral crystals during the spontaneous evaporation of a hydrochloric acid solution of the white oxid, it having also appeared that, in the manufacture of the embalming fluid, the arsenic was used as white arsenic.

A very strong point was finally raised for the defense by the inability of the people's expert to state positively whether or not an embalming fluid of the above composition would diffuse as a whole through dead tissue, or its several parts would be imbibed at different rates of speed, the zinc portion becoming arrested by albuminoid material and being therefore outstripped by the arsenic, or *vice versa*. Experimental evidence upon this topic is entirely wanting, for although an investigation touching upon this subject was instituted in this laboratory, the results are not in such shape as to permit of their use in so important a case as a trial involving life. The first trial resulted in a failure of the jury to agree, and the second in an acquittal of the prisoner.

RENSSELAER POLYTECHNIC INSTITUTE,
JUNE, 1893.

LIMES AND LIME TREES IN THE LEEWARD ISLANDS.[1]

REPORT BY VICE-CONSUL GALBRAITH, OF ANTIGUA.

The date of the introduction of the lime tree into these islands is a matter of conjecture. So far back as 1791 it is recorded that large quantities of the fruit of this tree was exported from Dominica to England and America. It was not, however, until about the year 1850 that the systematic cultivation of the tree began by Dr. Imray in Dominica, and quite independently by the Messrs. Sturge in Montserrat. During the first decade of the existence of this industry little progress was made. However, it lived, and early in the sixties the demand for it began to increase, and the cultivation of the tree and the manufacture of lime juice has gone on slowly increasing up to the present time.

The area under cultivation in Montserrat this year will be about 1,200 acres, of which about 900 acres are in fruit-bearing trees. The industry is carried on in a more systematic manner in Montserrat than in any of the other islands of the group, the Montserrat Company having had for several years a competent chemist to superintend the manufacture of lime juice and to advise in the agriculture management of their orchards. The work he did is still bearing fruit, and to-day Montserrat is the chief seat of the lime industry of the Leeward Islands.

There is a considerable quantity of lime juice manufactured in Dominica, but there the orchards are smaller, and, with one or two exceptions, the same care is not exercised in the cultivation of the trees nor in the manufacture of the juice. The industry is, however, growing, and, if the government succeeds in forming roads through the island, it is expected that there will be a large increase in the cultivation of lime trees, as well cultivated lime orchards are said to pay a good return. It is impossible to estimate the area in lime cultivation in Dominica. There are no official returns, and the majority of cultivators do not plant in regular orchards, as is done in Montserrat.

In St. Christopher and in Antigua the cultivation of the lime is unknown. Neither of these islands manufactures lime juice for export. The few trees scattered over the islands supply the

[1] From U. S. Consuls Reports, No. 147.

inhabitants with sufficient fruit for their own use, which is used principally in making various beverages and for culinary purposes.

The trees are raised from seed in nurseries and transplanted when ten to eighteen inches high to the orchard, where they are planted in rows about fifteen feet apart, each acre requiring from 175 to 200 plants, light sandy loam soil being best suited to their vigorous growth. In Dominica, where the soil is rich, the lime tree attains its greatest height and yields the most fruit, a large juicy lime which is very rich in citric acid. A lime tree will grow in almost any soil, but the fruit is small, and the life of the tree is not so long as in rich, well-cultivated lands. From three to four years from the time of transplanting the tree begins to bear fruit; about five years, however, would be the average time for fruit bearing, and it continues to bear for over twenty years. From the seventh to the fourteenth year the tree is in full bearing condition. After this, if the orchard is to be continued, young trees must be planted to supply the place of the older ones as they wear out. The tree blossoms all the year if there be rain; but March and April are the principal flowering months, and the fruit begins to ripen in June, when the lime harvest begins, and reaches its height in August. From then on to December the yield decreases each month until February, when it ceases to yield fruit.

The largest crops are gathered in years in which the rainfall is heaviest. The average yield of fruit from an orchard in full bearing would be about sixty to eighty barrels (an ordinary flour barrel is employed in all orchards to guage the quantity of fruit) from an acre per annum. This could, it is believed, be greatly exceeded by careful cultivation and manuring. A barrel of fruit will yield from six to seven gallons of juice, and each gallon of sound, ripe juice contains from twelve to fifteen ounces of citric acid.

The tree is subject to blight, which causes much trouble and materially affects the yield of fruit. No efficient remedy has as yet been found for this evil. With better cultivation and manuring, I have no doubt this would be remedied, as only the weak and sickly trees appear to suffer.

The fruit when ripe falls to the ground and is collected by women and children and carried to the works, where it is measured by an overseer, who credits each person with the amount collected each day; and on Saturday the quantity collected by each gatherer is paid for at the rate of from six to twelve cents per barrel, according to the scarcity of the fruit and the distance of carriage.

The produce exported from a lime plantation is as follows: Raw and concentrated lime juice, green and pickled limes, and essential oil.

Raw lime juice is simply the juice from good, sound, ripe fruit carefully preserved in casks. For the best quality the limes are crushed between the rollers of a mill. Old cane mills are usually employed for this purpose. The first two rollers are carefully adjusted to admit the lime; the second and third usually extract all the juice, which is then run into casks and is ready to ship. Most of the raw lime juice is sent to the English market.

In the manufacture of concentrated lime juice the crushing is done in the same manner as for raw lime juice. The fruit for concentration is not selected as for raw lime juice. On plantations where raw is manufactured the fruit which is unfit for manufacturing into raw lime juice is crushed and manufactured into concentrated lime juice. This process consists in boiling the juice in open pans, such as are used in the manufacture of muscovado sugar, until it is reduced to from six-eighths to one-tenth of its volume; it is then a black viscid fluid containing from 80–100 ounces of citric acid per gallon. When the juice has been concentrated to the desired strength, it is run into second-hand beer casks and shipped principally to the New York market.

The export trade in green limes is very small, and is not increasing; the small quantity which is shipped goes to the English market. The fruit is carefully selected, picked from the trees, wrapped in paper, as is usually done with oranges, packed carefully in crates, and shipped.

Another form in which the fruit is exported consists in selecting good, sound, ripe limes and placing them in casks, over

which is poured salt water or strong brine. The cask is then made perfectly tight and exported. Limes preserved in this manner are invariably sent to Boston. The brine has to be changed frequently during the process before the fruit is properly pickled. The quantity exported in this manner is very small, and, like the export of green limes, is not increasing.

I can not get figures showing the quantity exported in this manner, but believe the number of barrels or casks must be very few.

Essential oil, another valuable product obtained from the lime, is made largely on the Montserrat Company's estates and on a number of estates in Dominica. There are two kinds of essential oil of limes: the hand-made, which is the most valuable; the other, an oil procured by distillation. The hand-made commands a much better price, as its perfume is not effected by the heat necessary in distillation. The common mode adopted of extracting this oil from the lime consists of the use of a shallow concave metal plate shaped like an ordinary saucer, in which are studded a number of blunt copper spikes, from the center of which there is a tube, into which the oil runs as it escapes from the rind of the lime. The tube serves as a handle, and the lime is gently and quickly rolled over the blunt copper spikes until all the oil sacs are burst, and the oil escapes and runs into the tube. When the tube is full, the oil is poured into bottles and securely corked. Women are generally employed at the work, and they select only the finest fruit, which yields the greatest quantity of oil. The limes so used are then put through the mill for the manufacture of lime juice. When the bottle is full, it is allowed to stand for some time until the water and other impurities settle. The oil is then carefully drawn off and filtered as it is run into tinned copper vessels ready for export. Most of the oil exported from Dominica is manufactured by distillation from the lime juice which leaves the mill. It is very much inferior to handmade. It is chiefly employed now for scenting soaps and in the manufacture of common essences and perfumes. There are other modes adopted of procuring essential oil from limes; but, as they are not generally adopted by the majority of manufacturers either in Dominica or Montserrat, I do not think it necessary to describe them.

There is no doubt but that great improvements could be made both in the cultivation of the limes and the manufacture of its products if more scientific methods were adopted, but as long as the present way pays there is no hope of any improvements. The great majority of those engaged in the industry lack capital and are unable to make the improvements they see necessary, and, being unable to borrow, continue to run in the old grooves until the industry becomes unprofitable and they are forced to yield to lands which are not so rich, but which are cultivated by men who have the energy and capital to make inferior lands yield better than these islands, which are so well adapted for the cultivation of the lime.

There are no local buyers in any of these islands; consequently manufacturers ship their produce to either the English or New York market. The price is about the same in both places, but I am told the results from New York were slightly better than those from England. For the last two years many of the Dominican shippers have been sending their produce to the English market, owing to the New York purchasers having deducted from the sales the cost of freight and other charges, which formerly were paid by the purchaser.

The average shipments from Montserrat for the last five years were as follows: Raw lime juice, 800 puncheons of 120 gallons each; concentrated, 200 casks of fifty-four gallons each; green limes, 1,000 boxes; pickled limes, 300 barrels; essential oil, 2,500 pounds.

UNITED STATES CONSULATE,
    ANTIGUA, JULY 20, 1892.

NOTES UPON THE COMPOSITION AND SOME PECULIARITIES OF MULE'S MILK.

BY A. B. AUBERT, M. S., AND D. W. COLBY, B. S.

The animal from which the milk was obtained is the property of Mr. McLaughlin, railroad contractor, and is now worked, singly or with mate, on the construction of the Bangor and Aroostook railroad; is about eleven years old; weighs 1,100 lbs.; usual feed, hay and oats of good quality.

The mule showed no signs of heat previous to or at the time of milking; was milked several times a day giving about two quarts of milk in all. Two samples of milk were received at an interval of about three weeks, the flow of milk having begun about six weeks previous to the sending of the first sample.

When received, the milk was of a pure white color without yellowishness, of alkaline reaction, which upon being kept in a cool room, it only lost on the eighth day, becoming slightly acid. In spite of this change in reaction no curdling as exhibited by cow's milk took place, but simply the separation of a very fine flocculent, floating coagulum. The fat globules generally proved rather small; approximately ten per cent. averaging 0.001 mm. in diameter, forty per cent. from 0.0018 to 0.0037 mm., forty per cent. varied from 0.0037 to 0.0092 mm., the remainder running from 0.0092 to 0.0222 mm. and over.

A column of milk allowed to stand in a cool place for three days gave a separation of cream equal to one-seventeenth of the total height of the column. In the first sample of milk it was practically impossible to precipitate the casein with dilute acetic acid and carbonic anhydride.

By treating the milk with seventy per cent. alcohol a white, fine, flocculent precipitate was obtained, which upon being filtered and washed with seventy per cent. alcohol, strong alcohol, and lastly ether, dried and weighed, gave 2.52 per cent. and 2.17 per cent. of albuminoids, while by Kjeldahl's process 2.94 per cent. of albuminoids were obtained, the factor used being 6.25.

The albuminoids of the second sample exhibited rather different properties from those of the first sample, precipitating more readily by the addition of dilute acid.

This milk was diluted with fifteen times its own volume of water, very dilute acetic acid added, carbonic anhydride was passed through for twenty-five minutes and it was then set away in a cool place for forty-eight hours. A precipitate of casein was obtained which proved most difficult to filter and wash. The results obtained were 2.33 per cent. and 1.92 per cent., while the results by a method similar to Wanklyn's were 2.21 per cent. and 2.42 per cent. for total albuminoids. This would

indicate that the quantity of albumen could not be greater than 0.5 per cent., if as much.

<div align="center">RESULTS OF ANALYSIS.

SAMPLE NO. 1 (SPECIFIC GRAVITY AT 15°, 1.032).</div>

	Per cent.
Total solids	10.65[1]
Fats	1.86[1]
Albuminoids	2.94[1]

COMPLETE ANALYSIS OF SAMPLE NO. 2 (SPECIFIC GRAVITY AT 15°, 1.033).

Analysis No.	I, per cent.	II, per cent.	III, per cent.	IV. per cent.
Total solids	10.92	10.86	10.81	10.83
Albuminoids	2.21	2.42	....	....
Fats	1.99	1.97	2.30	2.25
·Sugar	6.07	5.96	....	....
Ash	0.52	0.53	....	....

I and II by A. B. Aubert; III and IV by D. W. Colby.

The fat in III and IV was extracted by petroleum benzene, which usually gives higher results than by ether extraction.

The only other American analysis of mule's milk which has come to our notice is that by E. F. Ladd (*Agricultural Science*, **1**, 108).

Below is given the composition of mule's milk as well as that of the mare and ass. The similarity is very apparent.

	Mule's milk. Average of analyses I and II. per cent.	Mule's milk. Results of E. F. Ladd. per cent.	Average composition given in "*Die Milch*." by Hermann Scholl. Ass' milk. per cent.	Mare's milk. per cent.
Water	89.14	91.59	89.64	91.00
Albuminoids	2.31	1.64	2.22	1.99
Fat	1.98	1.59	1.64	1.18
Sugar	6.04	4.80	5.99	5.31
Ash	0.53	0.38	0.51	0.43

Mare's milk, like that of the mule, is quite alkaline, remaining so for some time. It coagulates with difficulty, giving a very fine flocculent coagulum. The fat globules of ass' milk resemble those of mule's milk, being on the average very small.

MAINE STATE COLLEGE,
ORONO, MAINE.

[1] By D. W. Colby.

THE CHARACTERISTICS OF GLUCOSE SYRUPS.

BY W. E. STONE AND CLINTON DICKSON.

Since the examination of glucose and glucose syrups made from starch instituted by the National Academy of Sciences and reported upon in 1884, not much has been published in this country relating to these products. By reason of improvements in the processes of manufacture, however, some changes in the general composition of these materials might reasonably be expected.

The report referred to assigns the following composition to three samples of syrups.[1]

	I.	II.	III.
Dextrose	36.5	36.5	39.0
Maltose	19.3	7.6	....
Dextrin	29.8	40.9	41.4
Water	14.2	15.3	19.3

We have examined eleven samples of glucose syrups from as many different sources, obtained in the local retail market, representing the ordinary range of quality and at prices varying from thirty-five to sixty-five cents per gallon. In these samples we have determined density, percentages of moisture, crude ash and sulfuric acid anhydride, the relative reducing power before and after inversion, and the specific rotation before and after inversion and also after fermentation. These data are shown in the accompanying table.

Sample Number.	Specific Gravity.	Per cent. of water.	Per cent. of ash.	Per cent. of SO_3.	Relative reducing power.	Relative reducing power after inversion.	Specific rotation.	Specific rotation after inversion.	Specific rotation after fermentation.
I	1.417	20.8	0.72	0.022	39.06	40.99	98.81°	91.30°	10.90°
II	1.364	23.3	0.96	0.017	40.49	42.73	91.10°	82.49°	11.22°
III	1.389	26.0	1.12	0.030	39.68	46.29	79.76°	74.39°	10.21°
IV	1.390	23.2	0.84	0.025	36.76	59.52	85.23°	72.78°	10.61°
V	1.434	20.6	1.18	0.016	36.17	42.01	99.37°	92.21°	13.36°
VI	1.403	21.4	0.88	0.019	30.39	33.62	97.88°	86.36°	10.47°
VII	1.389	24.4	1.13	0.023	41.74	44.87	85.21°	78.34°	9.00°
VIII	1.409	24.8	1.21	0.023	29.04	42.68	92.08°	87.98°	11.53°
IX	1.404	23.6	0.69	0.024	37.45	40.00	98.46°	93.67°	12.99°
X	1.401	23.3	0.94	0.023	38.31	46.73	85.86°	76.13°	10.99°
XI	1.405	23.7	0.90	0.016	42.91	43.86	91.33°	89.13°	13.03°
	1.401	23.2	0.96	0.0216	37.46	43.93	91.37°	84.07°	11.30°

[1] Report on Glucose, Washington, 1884, p. 22.

No attempt has been made to ascertain the proportional amounts of dextrose and maltose present, since it is altogether probable that the proposed methods yield misleading results.

These syrups, on account of their peculiar nature, require special manipulation which, so far as it departs from the ordinary methods, is briefly explained in the following.

Specific Gravity.—It is impracticable, if not impossible, to obtain the specific gravity of these syrups accurately by ordinary methods owing to their viscosity and density. For this purpose we have resorted to dilution as proposed for bodies soluble in water.[1] A given weight of the syrup is dissolved in distilled water to a volume of 100 cc. The density of this solution being determined by the Westphal specific gravity balance we have

$W =$ weight of syrup employed

$w =$ weight of 100 cc. of the solution of same

Then $D = \frac{w}{100-(w-W)}$

For example, ten grams of syrup (W) are diluted to 100 cc., the density of which is found to be 10.35. The weight of the 100 cc. is therefore 103.5 grams (w), of which ten grams consists of syrup, leaving 93.5 grams or cc. as the weight or volume of water employed. The ten grams of syrup, therefore, occupy the same volume as 6.5 grams of water, and its density is $\frac{10}{6.5}$ or 1.583+. This method, while not yielding absolute results, is sufficiently accurate for comparative purposes. The variations between the samples were from 1.364 to 1.434.

Water.—To evaporate a sample of syrup to constant weight is not easily accomplished, and requires such long continued heating that other changes are to be feared. We have employed the method proposed by Wiley[2] which involves mixing the weighed syrup with weak alcohol and a weighed amount of clean sand, heating over a water bath with occasional stirring until dry, the addition of five cc. of strong alcohol, drying a second time over boiling water, and finally in the air bath at 100° C. for one-half hour. For samples weighing three to five

[1] *Allen's Commercial Organic Analysis*, 1, 209.

[2] *Allen's Commercial Organic Analysis*, 1, 306.

grams this operation occupies about three hours. The varia-
tions were from 20.6 to 26 per cent. of water.

Ash.—The determination of crude ash in sugars and syrups
by direct ignition is attended by the difficulty that these
materials upon carbonization puff up to a large volume, which
becomes unmanageable if the sample exceeds a very small
weight. The following method was used successfully: A
beaker containing a sufficient amount of the syrup and a
small pipette is weighed accurately. The pipette is filled from
the syrup and closed at the upper end with a bit of rubber
tubing and a screw pinch-cock. This is suspended over a
weighed platinum dish heated to redness and on slightly releas-
ing the pinch-cock the syrup flows out drop by drop. The
speed is so regulated that each drop is carbonized and in part
incinerated before its successor falls. When sufficient syrup
has been run in, the pipette is returned to the beaker and the
loss of weight ascertained. The partially burned mass is ex-
tracted with water, the residue incinerated at high temperature,
and finally to it the watery extract is added and the whole
brought to dryness and weighed as crude ash. In these sam-
ples the amount of ash varied from 0.69 to 1.21 per cent.

Sulfuric Acid.—In all samples a trace of sulfuric acid could
be recognized with barium chlorid. This did not appear to be free
acid, but probably represents the solubility of the calcium sulfate
resulting from neutralizing the acid used in "converting" the
starch. The amounts found were very small, varying from
0.016 to 0.024 of one per cent.

Relative Reducing Power.—The action of glucose syrups upon
Fehling's solution is due to at least two reducing sugars, dex-
trose and maltose. The results thus obtained are therefore not
to be ascribed to any single sugar. They show indirectly the
proportion of non-reducing substances of the nature of dextrin.
The numbers presented here give the amount of reduction as
compared with pure dextrose, or what is the same thing, the
dextrose equivalent of the reducing sugars present, and these
numbers vary from 29.04 to 42.91.

For inversion, five grams of the syrup were diluted to 200 cc.,
received ten cc. of concentrated hydrochloric acid, and the whole

maintained at 60°–70° for one-half hour. The acid was then neutralized with sodium carbonate and the solution filled up to the 250 cc. mark. The reducing power was found to be appreciably increased in each case by this treatment. The least increase was 0.97 and the greatest, 22.76. In this latter there was originally upwards of sixty per cent. of dextrin-like substances, and seventeen per cent. remained unchanged by the inversion process. It is noteworthy that this syrup commanded the highest price.

Specific Rotatory Power.—The three chief constituents of glucose syrups, dextrose, maltose, and dextrin, all rotate the plane of polarized light strongly. The specific rotation of such a syrup therefore reveals of itself nothing concerning the proportions of these substances. Inversion by converting dextrin and maltose into dextrose lowers the specific rotation. Fermentation by removing the dextrose and maltose leaves only the dextrin-like bodies to exert an influence on polarized light. This latter fact might be turned to account in determining these three substances when present in the same material were it not for the fact that what is known as dextrin appears to have no constant specific rotation. To determine, however, the rotatory power of the original syrup, the same after inversion and again after fermentation furnishes an interesting means of comparison between samples. The specific rotation of the syrups under discussion varied from 78.90°–99.37°. Inversion diminished these numbers from 4.1°–12.45°. Fermentation reduced the rotation markedly, but the effect of the dextrin-like bodies was still appreciable, the different samples still showing a specific rotation of 9°–13.36°.

The variations in these samples are not so extreme as to forbid averaging the results. It is obviously unwise to draw general conclusions from so small a number of analyses although it is hardly probable that a more extensive examination would reveal great variations. With these qualifications these syrups are characterized by a density of about 1.4, a water content of about twenty-three per cent., the ash materials are less than one per cent., and the residue from the acid used in manufacture is hardly more than a trace. The reducing sugars are equivalent

to about thirty-seven per cent. of dextrose, which is capable of increase by further use of acid, due to inversion of maltose or dextrin or both. They rotate the ray of polarized light strongly to the right which is decreased by inversion and an appreciable rotation persists after fermentation.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNI-VERSITY.—NO. 4.]

CHEMICAL COMPOSITION OF SIX CEREAL FOOD PREPARATIONS.

BY W. E. STONE AND FRED. McBRIDE.

Commercial food articles prepared from the cereal grains have become numerous and popular. In their manufacture certain parts of the natural grains are removed, retaining those portions of most attractive and appetizing properties. Just what effect the rejection of certain parts of the grain and reten-tion of other parts may have upon the comparative food value of the product cannot be exactly foreseen. The rejected parts are usually the hulls and coatings of the grain which, although less easily digested, are supposed to be especially rich in nitrogenous and ash materials. On the other hand the starchy parts of the grain, being white in appearance and easily cooked, are retained.

We have thought the matter of sufficient interest to warrant an examination of some typical sorts of these products. We have selected six on sale by local retailers, two from each of the cereal grains, wheat, maize, and oats.

Their composition, as ascertained by the ordinary accepted methods, is as follows:

	Moisture, per cent.	Composition of dry matter.				
		Ash, per cent.	Nitrogen.	Crude fiber, per cent.	Fat (ether extract), per cent.	Nitrogen-free extract, per cent.
From wheat:						
"Breakfast Food"	9.8	1.66	2.67	1.87	1.80	77.98
"Farinose"	9.8	1.14	2.99	0.96	2.46	76.76
From oats:						
"Nudavene"	8.8	1.94	3.59	1.50	9.28	64.85
"Rolled Avena"	7.8	1.36	3.22	1.35	7.73	68.47
From maize:						
"Cerealine"	8.1	0.52	2.39	0.64	1.27	82.64
"Snowflake Hominy"	6.8	0.47	2.32	1.01	0.62	83.40

For comparison the average composition of the entire grains as compiled by Jenkins and Winton[1] is given. These are averages of all complete analyses of samples of American origin which were available as follows: Of wheat, all varieties; of oats, all varieties; of maize, of "dent" varieties, although these differ inappreciably from the "flint" varieties in composition.

	Ash, per cent.	Nitrogen, per cent.	Crude fiber, per cent.	Fat (ether extract), per cent.	Nitrogen-free extract, per cent.
Wheat	2.0	2.12	2.0	2.3	80.4
Oats	3.4	2.11	10.8	5.6	67.0
Maize	1.7	1.84	2.6	5.6	78.6

Comparison of the above tables reveals that in each case the prepared products contain proportionally less ash and fiber and more nitrogen than the natural grains.

Of fat, the proportion has increased in the oat products, decreased in the maize, and in the wheat products has respectively lost and gained.

The nitrogen-free extract is less in the wheat products, greater in the maize products, and respectively greater and less in the oat products.

These changes in composition are on the whole in favor of the prepared products. In most cases also the physical condition is favorable to complete and rapid cooking.

In the two maize products, starch in a condition soluble in cold water was found, which would indicate that they had been partially cooked in preparation.

NOTE ON THE DISTRIBUTION OF ACIDS AND BASES IN A SOLUTION CONTAINING CALCIUM, MAGNESIUM, CARBONIC ACID, AND SULFURIC ACID, AND ON THE COMPOSITION OF MINERAL WATERS.[2]

BY C. H. BOTHAMLEY.

In examining the mineral waters of Askern, it was observed that the precipitate formed when the free carbonic anhydride was expelled by heat, or by the prolonged passage of a current of hydrogen, was almost pure calcium carbonate, and contained the merest trace of magnesium, although this element was

· present in considerable quantity.   It seemed of interest to investigate this matter further, with a view to obtain, if possible, some information as to the distribution of the acids and bases in a system containing calcium, magnesium, carbonic and sulfuric acid radicles, and water, and thus to throw some light on the constitution of mineral waters.   Experiments on this subject were therefore made in the Chemical Laboratory of the Yorkshire College in the early part of 1891, with the assistance of Mr. H. H. Mann, Brown Scholar of Yorkshire College.

Solid Magnesium Carbonate and Calcium Sulfate Solution.

(1) 0.5 gram of precipitated and well-washed magnesium carbonate was mixed with fifty cc. of water containing 0.0687 gram of calcium sulfate in solution, and the two were allowed to remain in contact for twenty-four hours at the ordinary temperature, with repeated agitation during the earlier part of the time. At the end of the experiment, the solution contained a very small quantity of calcium and a considerable quantity of magnesium, whilst the precipitate contained a considerable quantity of calcium carbonate.

(2) 1.0 gram of magnesium carbonate and fifty cc. of the calcium sulfate solution were allowed to remain in contact for twenty-four hours with occasional agitation.   Only the merest trace of calcium remained in solution.

(3) 0.5 gram of magnesium carbonate was treated in the same way with fifty cc. of water containing twice the quantity (0.1377 gram) of calcium sulfate.   At the end of twenty-four hours the solution contained only a trace of calcium.

(4) 1.0 gram of magnesium carbonate and fifty cc. of the stronger calcium sulfate solution.   At the end of twenty-four hours only a trace of calcium remained in solution.

It may be pointed out that the fact that a trace of calcium remains in solution does not show that the reaction is incomplete, because calcium carbonate is distinctly, though very slightly, soluble in water.   It follows that, in absence of free carbonic anhydride, calcium is completely precipitated from a solution of calcium sulfate by an excess of magnesium carbonate, magnesium sulfate going into solution.

Solid Calcium Carbonate and Magnesium Sulfate.

(5) 1.0 gram of precipitated calcium carbonate and fifty cc. of water containing 0.0525 gram of magnesium sulfate were agitated together at intervals during a day.

(6) 0.5 gram of calcium carbonate and fifty cc. of the magnesium sulfate solution were treated in the same way.

The result was the same in both cases. Although the calcium carbonate was present in large excess, only a mere trace of magnesium was found in the precipitate at the end of the experiment, and a mere trace of calcium in solution.

Magnesium Sulfate Solution and Calcium Carbonate Solution.

(7) Fifty cc. of the magnesium sulfate solution used in the preceding experiments, and fifty cc. of water containing 0.03790 gram of calcium carbonate, together with sufficient free carbonic anhydride to keep it in solution, were mixed and boiled for half an hour in a flask fitted with a reflux condenser. The precipitate contained but a minute trace of magnesium.

(8) 100 cc. of the magnesium sulfate solution and fifty cc. of the calcium carbonate solution were boiled together as in experiment 7. The precipitate contained only a trace of magnesium.

These experiments, in which the solutions and the precipitate that is formed are subjected to the action of heat, are open to some objection, but the results distinctly confirm those obtained with the solid carbonates.

(9) Fifty cc. of the magnesium sulfate solution and fifty cc. of the calcium carbonate solution were mixed, and a current of hydrogen was passed through the liquid for some time. The precipitate contained no magnesium.

(10) Ten cc. of water containing 0.1094 gram of magnesium carbonate and sufficient free carbonic anhydride to keep it in solution was mixed with 100 cc. of water containing 0.2754 gram of calcium sulfate, and a current of hydrogen was passed through the liquid. The precipitate that formed contained only a trace of magnesium, and consisted of calcium carbonate.

The complete precipitation of calcium by magnesium carbonate from a solution of calcium sulfate, and the absence of any distinct reverse action when calcium carbonate and magnesium

sulfate solution are brought together, seems to indicate clearly that in presence of water the sulfuric acid radicle combines with magnesium in preference to combining with calcium. The experiments in which the carbonates were at first in solution in presence of carbonic anhydride, and more especially experiment 9, lead to the same conclusion.

The heats of formation of the two sulfates in dilute solution are practically identical (calcium sulfate, 323.1 calories, and magnesium sulfate, 322.6 calories), although in the solid state the heat of formation of the calcium salt is distinctly the higher. The heats of formation of the two solid carbonates are : Calcium carbonate 269.2 calories, and magnesium carbonate 267.6 calories, but there seem to be no determinations of the heats of formation of the two carbonates in solution and in presence of an excess of carbonic anhydride. It is clear, however, that the existing thermochemical data afford no explanation of the facts observed.

It follows from these results that, if we put aside any question of ionic dissociation in solution, and represent mineral waters and similar solutions of calcium, magnesium, and the sulfuric and carbonic acid radicles as containing salts as such, the sulfuric acid should be regarded as combining with magnesium in preference to calcium, and not the reverse, as is generally supposed. In the case of the Askern waters, this view is supported by their therapeutic action.

THE INFLUENCE OF FREE NITRIC ACID AND AQUA REGIA ON THE PRECIPITATION OF BARIUM AS SULFATE.[1]

BY PHILIP E. BROWNING.

The fact demonstrated by Dr. F. W. Mar[2], in an interesting series of experiments, that free hydrochloric acid even in large quantities does not interfere with the complete precipitation of barium as sulfate when sulfuric acid is present in sufficient excess, but rather renders the precipitate more crystalline, and therefore more easily and quickly filtered, suggested a similar series of experiments having as their object an investigation of the influence of free nitric acid on the same precipitation.

[1] Am. J. Sci., 45, 399.
[2] Am. J. Sci., 40, 283. This Journal 5, 278.

Certain qualitative preliminary experiments showed a similar effect to that brought about by hydrochloric acid as regards the crystalline form and rapid settling of the precipitate. It therefore remained to determine whether the nitric acid present had any solvent effect upon the precipitate. Accordingly a standard solution of barium nitrate was prepared, free from alkali, by precipitating a soluble barium salt with ammonium carbonate, washing thoroughly with hot water and dissolving in nitric acid, care being taken to avoid an excess of the acid, and making up to measure. Definite portions of this solution were drawn from a burette into counterpoised beakers, and weighed as a check on the burette reading. Several precipitations of the barium in the form of sulfate were made, both in the presence of free hydrochloric acid and in neutral solution, and the mean of closely agreeing determinations was taken as the value of the standard solution. The mode of procedure in the testing was simple and may be outlined as follows : Into a counterpoised beaker a definite amount of the standardized solution of barium nitrate was drawn and the weight taken as before described, the amount of nitric acid to be used was then added, and the whole volume brought up to ninety cc. by the addition of water. This acid solution was then brought to the boiling point and ten cc. of the dilute sulfuric acid added, and the whole was allowed to stand for the length of time shown by the table before filtering on asbestos, igniting and weighing. It will be seen that the total volume of liquid taken in each determination was uniformly 100 cc., the percentage of acid by volume being thus easily regulated. In no case did the amount of barium salt present exceed 0.4 gram considered as the sulfate, and consequently the uniform amount of ten cc. of dilute (1 : 4 by volume) sulfuric acid employed was always enough to assure the excess which Fresenius[1] has shown to be necessary in the precipitation of barium as the sulfate in the presence of hydrochloric acid. By reference to Series I it is evident that in the presence of five per cent. of nitric acid very little solvent action is shown, and it appears also that the sulfate may be safely filtered after an hour's time. In the presence of ten to

[1] *Ztschr. anal. Chem.*, **30**, 455.

fifteen per cent. of the acid the solvent effect is very small when the solution is allowed to stand six hours or more. With twenty to twenty-five per cent. of acid present we find the solubility to be slightly increased, but even then the average loss is less than 0.001 gram.

SERIES I.

	BaSO₄ equivalent to Ba(NO₃)₂ taken, gram.	BaSO₄ found, gram.	Error in terms of BaSO₄, gram.	Averages, gram.	Time between precipitation and filtration, hours.	Per cent. by volume of strong HNO₃.	Total volume, cc.
(1)	0.2540	0.2336	0.0004—		12	5	100
(2)	0.2489	0.2483	0.0006—	0.0006—	12	5	100
(3)	0.2495	0.2489	0.0006—		12	5	100
(4)	0.2492	0.2482	0.0010—		12	5	100
(5)	0.2486	0.2483	0.0003—	0.0002—	6	5	100
(6)	0.2490	0.2490	0.0000		6	5	100
(7)	0.2555	0.2546	0.0009—	0.0006—	1	5	100
(8)	0.2538	0.2534	0.0004—		1	5	100
(9)	0.4067	0.4057	0.0010—		12	10	100
(10)	0.2540	0.2533	0.0007—		12	10	100
(11)	0.2492	0.2489	0.0003—	0.0006—	12	10	100
(12)	0.2493	0.2488	0.0005—		12	10	100
(13)	0.2494	0.2488	0.0006—		12	10	100
(14)	0.2492	0.2492	0.0000		6	10	100
(15)	0.2490	0.2489	0.0001—	0.0002—	6	10	100
(16)	0.2489	0.2484	0.0005—		6	10	100
(17)	0.2540	0.2524	0.0016—	0.0016—	1	10	100
(18)	0.2529	0.2515	0.0014—		12	15	100
(19)	0.2534	0.2522	0.0012—		12	15	100
(20)	0.2533	0.2531	0.0002—	0.0007—	12	15	100
(21)	0.2538	0.2532	0.0006—		12	15	100
(22)	0.2497	0.2490	0.0007—		12	15	100
(23)	0.2489	0.2487	0.0002—		12	15	100
(24)	0.2542	0.2528	0.0014—		6	15	100
(25)	0.2486	0.2486	0.0000	0.0006—	6	15	100
(26)	0.2492	0.2487	0.0005—		6	15	100
(27)	0.2547	0.2532	0.0015—	0.0015—	1	15	100
(28)	0.2489	0.2478	0.0011—		12	20	100
(29)	0.2486	0.2475	0.0011—		12	20	100
(30)	0.2548	0.2546	0.0002—	0.0008—	12	20	100
(31)	0.2548	0.2542	0.0006—		12	20	100
(32)	0.2496	0.2486	0.0010—		12	20	100
(33)	0.2539	0.2527	0.0012—		6	20	100
(34)	0.2488	0.2475	0.0013—	0.0008—	6	20	100
(35)	0.2497	0.2497	0.0000		6	20	100
(36)	0.2486	0.2477	0.0009—		12	25	100
(37)	0.2491	0.2490	0.0001—		12	22	100
(38)	0.2494	0.2484	0.0010—		12	25	100
(39)	0.2538	0.2535	0.0003—	0.0008—	12	25	100
(40)	0.2492	0.2484	0.0008—		12	25	100
(41)	0.2487	0.2471	0.0016—		12	25	100
(42)	0.3414	0.3407	0.0007—		12	25	100
(43)	0.2489	0.2481	0.0008—	0.0007—	6	25	100
(44)	0.2485	0.2478.	0.0007—		6	25	100

Having shown that free nitric acid even though present in considerable amount has only a slight solvent influence upon barium sulfate it seemed interesting to try the effect of the combination of nitric and hydrochloric acids mixed in the proportion to form aqua regia ($3HCl : 1HNO_3$). The experiments recorded in Series II show that aqua regia has even less effect as a solvent than nitric acid alone. In fact it seems to act like hydrochloric acid alone, which practically has no solvent effect, as shown by Dr. Mar's work previously cited.

SERIES II.

	BaSO$_4$ equivalent to Ba(NO$_3$)$_2$ taken, gram.	BaSO$_4$ found, gram.	Error in terms of BaSO$_4$, gram.	Averages, gram.	Time between precipitation and filtration, hours.	Per cent. by volume of strong aqua regia, (3HCl:1HNO$_3$).	Total volume, cc.
(1)	0.2539	0.2534	0.0005—		12	5	100
(2)	0.2540	0.2538	0.0002—	0.0002—	12	5	100
(3)	0.2490	0.2490	0.0000		12	5	100
(4)	0.2491	0.2492	0.0001+		12	5	100
(5)	0.2488	0.2484	0.0004—	0.0001—	6	5	100
(6)	0.3419	0.3421	0.0002+		6	5	100
(7)	0.2491	0.2487	0.0004—		12	10	100
(8)	0.2486	0.2482	0.0004—	0.0006—	12	10	100
(9)	0.2549	0.2539	0.0010—		12	10	100
(10)	0.2543	0.2538	0.0005—		12	10	000
(11)	0.2487	0.2485	0.0002—	0.0002—	6	10	100
(12)	0.3416	0.3415	0.0001—		6	10	100
(13)	0.3417	0.3420	0.0003+	0.0003+	1	10	100
(14)	0.2547	0.2544	0.0003—		12	15	100
(15)	0.2492	0.2492	0.0000	0.0003—	12	15	100
(16)	0.2489	0.2479	0.0010—		12	15	100
(17)	0.3412	0.3412	0.0000		12	15	100
(18)	0.3418	0.3417	0.0001—	0.0001—	6	15	100
(19)	0.3413	0.3412	0.0001—		6	15	100
(20)	0.3411	0.3402	0.0009—	0.0009—	1	15	100
(21)	0.2492	0.2484	0.0008—		12	20	100
(22)	0.2486	0.2480	0.0006—	0.0005—	12	20	100
(23)	0.2491	0.2485	0.0006—		12	20	100
(24)	0.3412	0.3411	0.0001—		12	20	100
(25)	• 0.3417	0.3418	0.0001+	0.0000	6	20	100
(26)	0.3417	0.3417	0.0000		6	20	100
(27)	0.3414	0.3404	0.0010—	0.0010—	1	20	100
(28)	0.2491	0.2485	0.0006—		12	25	100
(29)	0.1701	0.1697	0.0004—	0.0003—	12	25	100
(30)	0.1708	0.1705	0.0003—		12	25	100
(31)	0.1710	0.1710	0.0000		12	25	100
(32)	0.3415	0.3410	0.0005—	0.0003— •	6	25	100
(33)	0.3418	0.3418	0.0000		6	25	100
(34)	0.3412	0.3405	0.0007—	0.0007—	1	25	100

In this connection I append the results of a few experiments made to determine the effect of the presence of a considerable

amount of free nitric acid, on the precipitations of barium as sulfate in cases where certain substances are present which under ordinary conditions tend to hold up the precipitate. Fresenius[1] has demonstrated this property in the case of ammonium nitrate, Scheerer and Rube[2] have shown that metaphosphoric acid acts similarly, and Spiller[3] notes the same general effect where alkaline citrates are present. Series III shows the results obtained by precipitating definite portions of the standard solution of barium nitrate in the presence of stated amounts of the substances just mentioned. The total volume in every case was 100 cc., the amount of dilute sulfuric acid used ten cc., and the time between precipitation and filtration twelve hours. Upon filtering, igniting and weighing the barium sulfate, an excess of weight, due undoubtedly to contamination of the precipitate, was found. It became necessary, therefore, to purify the precipitate as first weighed in order to determine whether all the barium was actually precipitated or whether a partial loss was covered by the amount of included impurity. The method of purification employed was that successfully applied by Dr. Mar in the work previously mentioned. The contaminated sulfate, collected on paper and treated according to the familiar method (on account of the difficulty attending the complete removal of the precipitate from asbestos for purposes of purification), was dissolved in warm concentrated sulfuric acid, and evaporated quickly and without spattering by means of the Hempel burner, the barium sulfate being left after this treatment in coarse granular crystals. The crystallized sulfate was warmed with a little water containing a drop of sulfuric acid, filtered upon an asbestos felt contained in a perforated platinum crucible, the crucible and felt having been previously ignited and weighed.

SERIES III.

Impurity present to the amount of 5 grams.	$BaSO_4$ equivalent to $Ba(NO_3)_2$ taken, gram.	Apparent amount of $BaSO_4$ found, gram.	$BaSO_4$ after purification, gram.	Error after purification, gram.	Per cent. of strong HNO_3 by volume.
(1) Ammonium nitrate..	0.1710	0.1800	0.1702	0.0008—	10
(2) " " ..	0.3415	0.3440	0.3410	0.0005—	10
(3) " citrate..	0.3412	0.3442	0.3407	0.0005—	10
(4) Sodium citrate	0.1360	0.1730	0.1366	0.0006+	10
(5) Metaphosphoric acid	0.3461	0.3511	0.3470	0.0009+	10

[1] Ztschr. anal. Chem., 9, 62.
[2] Erdm., J. prakt. Chem., 75, 113–116.
[3] Chem. News, 8, 280, 281.

The results show that in the presence of nitric acid amounting to one-tenth by volume of the entire liquid these salts apparently do not interfere with the precipitation of the barium.

The entire work would seem to show that the presence of an excess of nitric acid or aqua regia amounting to ten per cent. by volume of the liquid treated is not only not to be avoided in estimating barium as the sulfate, but is actually beneficial. Ordinarily the advantage is found in the tendency of the precipitate to fall coarsely crystalline under the conditions. In certain special cases in which certain substances mentioned, which would otherwise exert solvent action, are present the precipitation is made complete. The contaminating effect of such substances when complete precipitation is induced may be corrected by dissolving the precipitate in sulfuric acid and recrystallizing by evaporation.

AN IMPROVED METHOD FOR THE SEPARATION QUALITATIVELY, OF MERCURY, LEAD, COPPER, CADMIUM, BISMUTH, ARSENIC, ANTIMONY, AND TIN FROM THEIR MIXED SULFIDS.[1]

BY ALEXANDER R. CUSHMAN, PH.D.

The necessity for a modification of the ordinary scheme in use for the qualitative analysis of the fifth and sixth groups, according to Fresenius's arrangement of the metals, has led me to propose the following as very satisfactory in its results. Yellow ammonium sulfid, $(NH_4)_2S_x$, converts the mixed sulfids of mercury and tin into a compound containing both of these metals, and which is readily soluble in water. The digestion with this reagent, which is necessary in the usual method of separation of the fifth and sixth groups, obviously introduces a complication which I have sought to remove.

In the method proposed, the usual precipitation of silver, mercurous salts, and lead by means of hydrochloric acid is assumed to have been made, and the filtrate, now acid, is treated with hydrogen sulfid gas in order to precipitate the sulfids of the fifth and sixth groups. The mixed sulfids are now warmed with yellow ammonium sulfid, and after digestion,

are filtered through a *dry* filter. The residue is then washed
with a ten per cent. solution of ammonium nitrate, which
removes the excess of yellow ammonium sulfid, but is
without effect upon the soluble compound of sulfids of tin and
mercury contained in the residue. This residue is now treated
with moderately diluted nitric acid, with the application of a
gentle heat, filtered and washed. The metals of the fifth group,
with the exception of mercury, will be found in the filtrate,
while in the residue there are contained mercuric sulfid and
metastannic acid.

This residue is finally treated with aqua regia to dissolve the
mercuric sulfid, and the remaining metastannic acid may be
filtered off and tested on charcoal by moistening with cobalt
nitrate and ignition in the outer blowpipe flame. The appear-
ance of the characteristic bluish-green color proves tin. Or, the
metastannic acid may be reduced to metallic tin by means of
zinc and platinum, then dissolved in hydrochloric acid and
tested with mercuric chlorid.

A portion of the tin will also be found in the solution of the
sixth group sulfids in yellow ammonium sulfid, and is there to be
separated in the usual manner.

HOW SULFATE OF MORPHINE IS MADE.[1]
BY J. CALVERT, PH.C.

At the session of the A. P. A. held in San Francisco in 1889,
I gave an account of how the Chinese prepare smoking opium.

I now propose to tell you how sulfate of morphine is prepared,
as we see it in the vials furnished to us by the American manu-
facturers.

Some years ago I was asked by William Geary, formerly of
Redington and Company, and now of the firm of Kirk, Geary,
and Company, of Sacramento, to investigate certain matters re-
garding opium, among others, the manufacture of sulfate of mor-
phine. The principal condition of Mr. Geary was that the pro-
duct should conform to the appearance and bulk of that of the
product of Powers and Weightman. I worked on the problem
for half a year, and at last gave it up, as I saw no solution of it.

[1] From the *American Druggist.*

Then Mr. Geary told me that he had certain information about a German chemist whose name I forget, who could give some notes on the subject. We wrote to him, and his reply exactly confirmed what had been told to me by my former partner, Professor Emlen Painter, as to what he had seen in Philadelphia in 1876, and which I thought at the time to be merely samples for exhibition—that is, bricks of morphine sulfate, perfectly white, and solid. He saw these bricks in the office of Powers and Weightman and when he told me of them I was amazed, as the only way in which I could imagine sulfate of morphine to be made was by simple solution and crystallization.

In the preparation of sulfate of morphine there are two things to be considered,—first, decoloration, second, form of product; and in order to give an idea of the whole process it will be necessary to commence with the raw material.

Opium in any quantity is exhausted with water. The resulting liquid is precipitated with an alkaline base, and crude morphine is the result. The crude morphine is taken up with sulfuric acid and water, filtered through animal charcoal, and brought to a density of $4\frac{1}{2}$ to 5 B. The crystallizing apparatus is a leaden tank, about six inches in depth, of any size to correspond with the amount of morphine sulfate. It is hinged on a frame and has an outlet, with a plug or faucet at the lower end for drainage. The solution being ready and the apparatus adjusted, the hot solution is run into the crystallizer.

The solution is stirred gently every few minutes until crystals · commence to form on the surface, and then, carefully stirring, when the solution has come to the right temperature, the morphine sulfate crystallizes suddenly into a solid mass.

The mass of crystals is allowed to repose for forty-eight hours, the plug at the lower end of the tank is removed and the mother liquor is allowed to run off, at first slowly, and afterward, by elevating the apparatus, the last of the liquor is removed. The drainage requires several days.

The crystals in the apparatus are then cut up into pieces of the shape of bricks, (commencing at the upper end) which are placed on an absorbent, and removed to a drying room.

Now comes a singular part of the process.

In ordinary crystallization a certain part of the coloring matter is retained in the crystals. In this case, when the morphine is crystallized as described, and dried in bricks, nearly all the retained coloring matter comes to the surface, so that when the bricks come out of the drying room the surfaces are brown, and in some cases almost black, showing that the coloring matter is eliminated. The next part of the process is to remove the colored part. This is effected by slicing off the dark portions, leaving the morphine sulfate perfectly white. The masses of crystals of sulfate of morphine (which I have heretofore described as bricks) are in a condition to be made into a merchantable article.

A very sharp knife and delicate hands will do it. The bricks are placed on a table and slices are cut off of them (about one-fourth inch each). These slices are gently crumbled in the hands (very gently). Thus they will accommodate themselves to the capacity of the usual bottles of the trade.

A CONTRIBUTION TO THE CHEMISTRY AND PHYSIOLOGY OF FOLIAGE LEAVES.[1]

By Horace T. Brown, F.R.S., and G. Harris Morris, Ph.D.

The investigation relates to the occurrence, relations and physiological significance of the starch, diastase, and sugars contained in foliage leaves.

The authors divide the subject into two parts: The first, dealing with the starch and diastase of leaves, is subdivided into the following sections,—(1) Introduction; (2) Historical; (3) The starch of the leaf, its determination, and the proportion it bears to the total products of assimilation; (4) The occurrence of diastase in the leaf; (5) The nature of the products of transformation of starch by leaf diastase; (6) The determination of the diastatic activity of leaves; (7) The periodic variation of the diastase of leaves; (8) Can leaf diastase act on solid starch? (9) How far is the disappearance of leaf starch due to living protoplasm? The second part treats of the sugars of the leaf, and consists of an historical section, and one dealing with the

[1] From the *Proceedings* of the London Chemical Society.

sugars of *Tropæolum majus*. The bibliography of the subject is summarized in an appendix.

The work originated in an attempt to discover the explanation of the conditioning effect of "dry hopping," *i. e.*, the addition to finished beer of a small amount of dry hops. This was ultimately traced to the presence in the hop strobiles of a small, but appreciable, amount of diastase, sufficient to slowly hydrolyze the non-crystallizable products of starch transformation left in the beer, and to reduce them to a condition in which they can be fermented by the yeast. In endeavoring to ascertain if this occurrence of diastase in the hop strobile was an isolated case, or a special example of a widely distributed property of vegetable tissue, the authors were led to inquire into the first formation of starch in the chloroplasts of the foliage leaf, the mode of its dissolution and translocation in the plant and the nature of the metabolized products.

The results obtained are regarded as entirely antagonistic to the assumption made by Sachs, that all the products of assimilation at some time take the form of starch.

Using the half-leaf gravimetric method devised by Sachs, the authors confirm his results as to the rate of assimilation, but they show that only a small portion of this assimilated material exists at any one time in the form of starch.

The starch in leaves was estimated by hydrolyzing it with suitable precautions, with the aid of diastase, and then determining the products of its hydrolysis in the usual way by means of the polarimeter and Fehling's solution. The fluctuations in the amount of starch in leaves under various conditions, and also in leaves plucked at different times in the day, have been determined by this method.

It is shown that Wortmann's recent denial that diastase plays any part in the dissolution and translocation of starch in leaves is incorrect. The authors prove that instead of leaves containing little or no diastase, every leaf examined by them contained sufficient diastase to transform far more starch than the leaf can have contained at any one time. In many cases sufficient diastase was present to hydrolyze an amount of starch many times the total dry weight of the leaf. The difference between

the authors' and Wortmann's results is chiefly due to the fact that whereas Wortmann examined the clear filtrate obtained by macerating the crushed leaves in water during a few hours, they have digested the air-dried and powdered leaf itself with soluble starch solution.

It is further shown that the products of the hydrolysis of starch by leaf diastase are identical with those formed by malt diastase, maltose having been directly separated from the leaves and its optical and reducing properties determined. Leaf diastase is not able to convert maltose into dextrose, but the leaf contains an enzyme capable of inverting cane sugar.

In the course of a large number of comparative determinations of the diastatic activity of various leaves, it was found that the amount of diastase varied greatly in different plants, and within narrower limits even in the same plant at different times. It is very high in the case of the Leguminosæ, the diastatic activity of *Pisum sativum* being between one-half and one-third of that of an average pale barley malt.

An attempt to ascertain if the fluctuations in diastase were in any way periodic, or were governed, as are the fluctuations of starch in the leaf, by any external conditions showed that any conditions which favor a decrease in the leaf starch result in an increase of the leaf diastase; for instance, leaves kept in darkness, either on or apart from the plant, show a marked increase in diastatic activity. In view of the results obtained in their former paper on the "Germination of the Gramineæ" (*Trans.*, *1890*, 458), the authors explain this by the assumption that as long as the conditions favor assimilation, the leaf cells are necessarily supplied with an abundance of newly assimilated materials in the form of sugars, more, in fact, than can be easily made use of or translocated, the excess of nutritive material being in part deposited as starch. At this period there is little or no elaboration of diastase by the cell-protoplasm, probably none at all in those cells in which starch deposition is actually going on. When the light fails and assimilation consequently falls off, the living cells speedily use up or translocate the excess of assimilated products, such as cane sugar, and begin to draw their supplies from the more permanent starch   To enable the

cells to do this effectually the somewhat starved protoplasm now commences to elaborate the needed diastase more rapidly, and the secretion of the enzyme becomes accelerated as the starvation point of the cell is reached, the secretion of diastase by the leaf cell being in fact like that of the embryo of the grasses, to some extent a phenomenon of starvation. Experiments confirmed this view.

Contrary to Wortmann's statement, it was found that under certain conditions leaf diastase can attack the solid starch granule, but attempts to obtain any evidence of the disappearance under the influence of the contained diastase of starch in killed leaves gave negative results, and the authors are led to the conclusion that the first stage of dissolution of the starch granule in the leaf is in some way or other bound up with the life of the cell. When, however, all the facts are considered and due weight given to (1) the constant and abundant occurrence of diastase in leaves, (2) to the apparent correlation of this diastase with the occurrence of starch, (3) to the remarkable periodicity of the rise and fall of diastase, and (4) to the correlation of this periodicity with the appearance and disappearance of starch, it is impossible to accept Wortmann's view that the dissolution of starch in the leaf is in no way conditioned by a starch-dissolving enzyme. On the contrary, the authors believe that their experiments establish beyond all doubt the physiological importance of diastase as an active agent in the dissolution and translocation of starch, not only in leaves, but also in the growing parts of all plants. As further evidence of this, the authors adduce the fact that maltose was found among the sugars of the leaf when the starch was disappearing.

Selecting the leaves of *Tropæolum*, experiments were carried out to ascertain the nature of the leaf sugars and the variations in amount and relative proportions at different times, and also for the purpose of throwing some light on the relation which each sugar bears to the primary assimilation products on the one hand, and to the leaf starch on the other, *i. e.*, to ascertain which are the true "up-grade" sugars from which starch is formed and which are the "down-grade" sugars resulting from the hydrolysis of starch.

The only sugars found were cane sugar, dextrose, levulose, and maltose. The total amount of the sugars is subject to great variations, and the relative proportion which they bear to each other is also very varied. The results obtained lead to the following conclusions: Cane sugar is the first sugar to be synthesized by the assimilatory processes. This sugar accumulates in the cell sap of the leaf parenchyma when assimilation is proceeding vigorously, and when the concentration exceeds a a certain point starch commences to be elaborated by the chloroplasts at the expense of the cane sugar. This starch forms a more stable reserve material than the cane sugar, and is only drawn on when the latter, more readily metabolized substance, has been partially used up. Cane sugar is translocated as dextrose and levulose, and the starch as maltose. From the invert sugar derived from the cane sugar, the dextrose is more readily used up for the respiratory processes, and possibly also for the new tissue building, than is the levulose; hence, in a given time more levulose than dextrose must pass out of the leaf into the stem.

DISCUSSION.

The president, after remarking that a more suggestive paper had never been brought under the notice of the society, referred to the statement made by the authors regarding the origin of the research as a striking illustration of the advantage to be derived from the association with our manufacturing industries of thoroughly qualified scientific men. A research originally commenced with the object of explaining a common brewery practice had not only afforded the required information, but in addition improved methods of analysis had been devised in the course of the work; and facts had been discovered which ultimately might serve as the basis for the interpretation of the manifold changes involved in the formation and degradation of carbohydrates in plants, and which also might largely contribute to the solution of purely theoretical problems concerning the nature of the carbohydrates. He was not prepared to allow the interpretation of the manner in which cane sugar was formed, that had been put forward by Messrs. Brown and Morris, to pass unchallenged. On a previous occasion, when

discussing their paper on the "Germination of the Gramineæ," he had suggested that perhaps cane sugar was formed from maltose, and not from dextrose and levulose, to unite which all attempts hitherto made had failed; that, in fact, one of the dextrose residues of maltose was converted into levulose, and that the compound thus formed underwent a change—an internal condensation—resulting in the production of cane sugar, the nature of which even yet is not understood, but which apparently does not contain aldehydic groups. The evidence now brought forward was, he thought, compatible with this view. Such a passage from maltose to cane sugar would be of advantage to the plant, as it would then have at disposal a material that was hydrolyzed more easily than maltose. The superior nutritive value of cane sugar might be due at least partly to this fact. Levulose perhaps played a special part in certain metabolic processes. It was well known to be much more sensitive than dextrose towards hydrolytic agents, the formation of levulinic acid being an instance of this, and it was not improbable that it was therefore of superior value in comparison with dextrose and other carbohydrates, because able to take part in some of the changes involved in the elaboration of tissue to which other carbohydrates on account of their stability were at least less readily amenable.

Mr. Thiselton Dyer said that he was much mistaken if this paper did not prove to be one of the most important contributions to the study of plant metabolism of the century. The problems involved are open to two lines of attack, the botanical and the chemical; neither in his opinion could lead to wholly satisfactory results. It was Mr. Horace Brown's singular merit that he had been able to combine both. His conclusions may therefore be expected to be convincing both to the botanist and to the chemist.

It was not too much to say that botanists have long waited for the work which Mr. Horace Brown and his colleague are doing and have done. A good many years ago Dr. Hugo Muller had pointed out to him how far in advance in these matters the botanical results were of those which chemists had reached. And to a botanist not the least interesting feature in

this paper was the frank recognition of the value, from a chemical point of view, of the classical work accomplished in this field by Sachs and Schimper. The botanical attack had for the time, however, gone as far as it could, and it awaited the chemical complement, which it is now in a fair way to receive.

The primary fact of plant assimilation is assumed. That is an outcome of protoplasm activity, the details of which we need not discuss. The result is generally admitted to be what we may call a "proto-carbohydrate." Now this substance reveals itself in a visible and derivative form, on the one hand in cellulose and on the other in starch. The deposition of the former is the work of the general protoplasmic body of the cell; that of the latter is, as far as we know, the special function of certain specialized protoplasmic corpuscles, known as plastids. Of these, botanists now recognize three separate groups—chloroplastids, chromoplastids, and leucoplastids. The latter are identical with the amyloplasts of Schimper. We now have reason to believe that these groups may be reduced to two—the colored and the colorless plastids. The chloroplastids in point of fact are only a particular phase of the chromoplastids. All alike possess the common property of determining the formation of starch granules. The more we know of these bodies the more remarkable are their properties. They appear to have their own independent method of multiplication by division. It is even probable that they are bodily inherited from one plant generation to another; and both Schimper and Lankester have hinted that they may be autonomous organisms leading a commensal existence with the plant whose physiological needs they so conspicuously subserve.

Nothing is so remarkable in the general survey of plant metabolism as the repeated passage of its products from the soluble to the insoluble form, and *vice versa*. He had long been of opinion that the key to the *modus operandi* of these tranformations is to be found in the action of enzymes, and had done his best to emphasize the view in an address which he gave to the British Association in 1888. But in science a merely theoretical view is of little value without a formal proof. And as regards the mode in which starch is brought into use, it

appeared to him that Mr. Horace Brown had for ever set that question at rest. The difficulties raised by Wortmann never weighed much with botanists, and Mr. Horace Brown had demolished them, as it seemed to him, for ever.

So far we were very grateful to the authors of the paper for clearing the way for us. But what follows was not at present free from difficulty. The botanical point of view was briefly stated by Sachs in the case of the sugar beet: Starch in the leaf, glucose in the petiole, cane sugar in the root. As he had pointed out in the *Kew Bulletin* for 1891, the facts in the sugar cane seem to be strictly comparable. Cane sugar the botanist looks on, therefore, as a "reserve material." He had ventured, in fact, to call glucose the sugar "currency" of the plant, cane sugar its "banking reserve."

The immediate result of the diastatic transformation of starch is not glucose, but maltose. But Mr. Horace Brown had shown in his remarkable experiments on feeding barley embryos that, while they can readily convert maltose into cane sugar,.they altogether fail to do so with glucose. We may conclude, therefore, that glucose is, from the point of view of vegetable nutrition, a somewhat inert body. On the other hand, evidence is apparently wanting that maltose plays the part in vegetable metabolism that might be expected of it. Its conversion into glucose may be, perhaps, accounted for by the constant presence in plant tissues of vegetable acids. But, so far, the change would seem to be positively disadvantageous. Perhaps glucose, in the botanical sense, will prove to have a not very exact chemical connotation.

That the connection between cane sugar and starch is intimate is a conclusion to which both the chemical and the botanical evidence seems to point. And on botanical grounds this would seem to be equally true of its connection with cellulose.

It must be confessed that the conclusion that cane sugar is the first sugar to be synthesized by the assimilatory processes is one which is rather startling to the botanist. It seems hard to reconcile with its probable high chemical complexity and with the fact that botanically it seems to stand at the end and not at the beginning of the series of metabolic change.

A few words must be said in conclusion on the references made by Mr. Horace Brown to the part played by protoplasm.

" Protoplasmic continuity " is a great induction, to the establishment of which the work accomplished by Mr. Gardiner at Kew had, in great measure, contributed. He was, however, inclined to approach with caution the use Mr. Horace Brown had made of it. He was far himself from thinking that it can at present be relied on to explain the "rapid translocations" of metabolites. For his part, for various reasons, he had been content to think that where a tract of tissue becomes the seat of an enzymic action (as in germination), the continuous protoplasm may act as the means of transmission of an enzyme from cell to cell, or even of some influence by which an enzyme is set free from a zymogen. But he doubted the evidence at present being sufficient to accept it as the path of the bodily transmission of a metabolite.

The resistance which living protoplasm presents to the ordinary physical processes of diffusion is an old difficulty. Invoking the continuity of protoplasm did not in his opinion materially dispose of it. But, on the other hand, it must be remembered that the cell, which is the active seat of metabolic change is in a state of tension; and the opposition offered by protoplasm to diffusion is mitigated by the fact that it can not be invariably regarded as a continuous membrane, but is itself under such circumstances frequently porous and subject to physical permeability.

He must finally relieve his mind of an idea that had often occurred to him about protoplasm as the seat of chemical changes of immense importance. In the laboratory we are accustomed to deal with organic substances as comparatively stable. Their molecular up-building or synthesis, when effected by the chemist, is generally difficult and circuitous. He thought we must accustom our minds to the fact that in the "protoplasmic field" these processes may be much more easily accomplished. Under such circumstances it appeared to him that the molecules of various substances may be subject to soliciting influences of the nature, perhaps, of solution, which, without altering their chemical identity or constitution, may make their

chemical transformation far more easy to accomplish than it is by ordinary chemical means. He was not desirous of violating chemical order or law, or of claiming for protoplasm any "vitalistic" properties. But at the same time it would be absurd to shut our eyes to the unique properties that protoplasm possesses or to refuse to admit that it may, in consequence, have the power of conditioning chemical change in a probably unique manner. At any rate he might point to the facility with which, in the field of organic nature, chemical change seems to be effected, and to the profusion of products which result from it. What nature, with the aid of protoplasm, appears able to effect with extreme facility the chemist can only follow with laborious difficulty.

No doubt it may be said that this is to introduce a new and unknown quantity into chemistry—a biological element in fact. Why not? He could conceive that the path of chemical change in the organism may be conditioned by adaptive requirements, by natural selection in fact, and that the substances which now dominate the chemistry of plant life may have attained their prominence, not so much in obedience to unselective chemical change as to the requirements of plant life. Enzymes, for example, may in the first place have been mere proteid derivatives of protoplasm. But their peculiar properties of bringing about fermentative change may have rendered possible, and, therefore, stereotyped, the whole series of plant metabolism, with its singular alternation of soluble and insoluble products.

Dr. D. H. Scott said that since the publication of Schimper's paper of 1885, the idea that starch is not the first product of assimilation had been familiar to botanists. In fact, Sachs himself had never said that it was so, but had spoken of starch as the first easily demonstrable product. Botanists generally supposed, with Schimper, that glucose or some similar sugar is a prior product to starch. Messrs. Brown and Morris's conclusion that cane sugar is first formed was an entirely new departure.

The paper proved that the starch formed by the chloroplasts is precisely the same thing as starch formed by leucoplasts,

namely, a reserve food substance, and nothing more. So far, the chloroplast is physiologically as well as morphologically identical with an amyloplast destitute of chlorophyll. But the chloroplast has the further, quite distinct, function of forming a carbohydrate, in the first instance, from inorganic materials.

Messrs. Brown and Morris had shown what brilliant results might be attained when skilled chemists devoted themselves to physiological problems.

Professor Green, after alluding to the author's theory of the improbability of all the carbonaceous material of the plants' food passing through the starch stage, referred to the possibility that at the same time that the formation of carbohydrate was taking place there might be a coincident formation of vegetable acids, part of the increase in weight of the leaf being so accounted for; thus from formaldehyde it seemed possible to pass to formic acid, and subsequently to higher acids such as the parenchyma of the plant contains.

He asked also whether in noticing the variation of the diastatic power of the leaf at different times of the day the authors' attention had been directed to a possible inhibitory effect of light upon its action. The quantity might vary as the author suggested, but it was at least possible that with a constant quantity the diastatic action might be much less in the day time, owing to the diastase being unable to work in sunlight.

In this connection, Professor Marshall Ward's experiments on the bactericidal action of certain rays were significant, as they indicated a possibility of protoplasm being directly affected by these rays. If protoplasm itself is so interfered with, might not its enzymes also be disturbed by the same influence?

The views of Böhm and Baranetzky as to the diastase being used up in course of its activity are not in accord with the opinion of most workers on the enzymes. As Mr. Brown appeared to endorse these views to a certain extent, could he quote experiments clearing up the point? O'Sullivan's experiments on invertase (*Trans.*, *Oct.*, *1890*) pointed to a directly opposite view.

In criticizing Wortmann's method of preparing his extracts, Mr. Brown had pointed out the difficulty of extracting enzymes by water. There was another solvent which, in many cases, offered great advantages, *viz.*, a five per cent. solution of common salt. The greater power of this as an extractive was possibly connected with the frequent association of the enzymes with globulins.

Dr. Lauder Brunton observed that the paper opened up very many new lines of inquiry. It threw a light not merely on vegetable physiology and chemistry, but on the physiology of animal life and also on that of the lowest organisms which could hardly be reckoned either as animal or vegetable. He thought that perhaps animal life in its turn might throw a light on vegetable physiology, and instanced the close resemblance that existed between the storage of glycogen in the liver of animals during digestion with its subsequent conversion into sugar and the temporary accumulation of starch and its subsequent removal from the leaves of plants. In the pancreas of an animal, one of the enzymes which was present in the juice of the secreting gland and also in its substance appeared to be entirely absent from the gland of fasting animals. This absence is only apparent, for the enzyme is really present, not in an active condition, but in the form of a zymogen. From this zymogen the active enzyme may be liberated by treatment with dilute chlorhydric acid and subsequent neutralization. He was desirous to know whether any such zymogen had been found in leaves where starch was accumulating. The pancreas of animals was also remarkable in this particular, that while the gland was pouring into the intestines a juice which converts starch into sugar, it was also pouring through the lymphatics into the blood an enzyme which destroys sugar. He thought it possible that more than one enzyme might be present in the leaves of plants, and was anxious to know whether any observation had been made as to the presence of an enzyme in the plant which could decompose sugars.

A DIGESTION FLASK FOR OBTAINING THE ACID SOLU-TION IN SOIL ANALYSIS.

By Harry Snyder.

In soil analysis the directions given by Professor Hilgard for obtaining the acid solution are to weigh out five grams of the soil into a porcelain beaker, add fifty cc. hydrochloric acid (sp. gr. 1.115, etc.) and digest for five days. Even with the utmost care in securing tight fitting covers for the beakers, a portion of the solution is evaporated and must be replaced from time to time. This is open to objection, since the acid is continually changing its strength, and the result is that the soil is acted upon by acid of different strength than that originally intended. This objection was noted by Professor Kedzie, of the Michigan Agricultural College, in his report to the Association of Official Agricultural Chemists in 1891, in which he recommended the use of glass-stoppered bottles, the stoppers to be secured by wiring before the bottles were immersed in the water bath.

In using stoppered bottles it is difficult to obtain bottles that will withstand so high a pressure for so long a time, and it requires a very perfect fitting stopper to prevent any interchange between the hot solutions in the water bath and the acid in the bottles.

During the past year the writer has had in use a digestion flask that has obviated all of the difficulties of both the covered beaker and the stoppered bottle. The flask with its ground glass stopper is shown in Fig. 1. The flask has a capacity of 100 cc. The ground glass stopper is provided with an exit tube that can be connected with a small glass tube or a condenser. The soil is weighed direct into these digestion flasks, and the proper amount of acid added. The flasks are then placed in the water bath and connected with the condensers. At the end of the fourth day the solution and insoluble residue is transferred to a casserole, and all of the remaining determinations made in the usual way.

Fig. 1.

A compact form of condenser can be made from a galvanized iron pail by perforating the bottom with holes a little larger than the glass tubes that are to be inserted, and making the joints water-tight by means of rubber tubing. Long glass tubes can be used without any condensing apparatus. A cover is also provided for the water bath with small openings to allow the condensing tubes to pass through. The appearance of the digestion apparatus when in working operation is shown in Fig. 2. A small bath of eight inches diameter will accommodate six or eight extraction flasks.
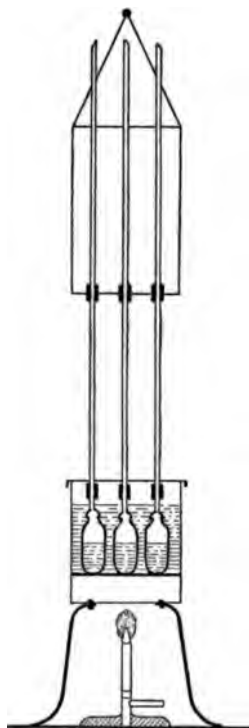
At the close of the operation the weights of the flasks with their contents are nearly identical with the initial weights, which shows that the losses are very slight and that the acid has not materially changed in strength during the four days' digestion. When the flasks are placed in the water bath and connected with the condensers, the digestion requires but little attention. There are no fumes given off in the laboratory. There is no change in the strength of the acid solution. A constant temperature can be secured, and all of the necessary and essential conditions are under control which can not be said of the porcelain beaker. The only objection that can be urged against extraction flasks is the possibility of the glassware giving up some of its alkali. Stoppered bottles are open to this same objection. Blank determinations, however, show that the amount of alkali given up from good hard glass flasks and bottles is a very small amount.

The digestion flask, stoppered bottle, and porcelain beaker have been given a number of trials and comparative tests, and a few of the typical results are given in the following table:

FIG. 2.

Kind of sample.	Method.	Total insolu-ble.	K₂O.	Na₂O.	CaO.	MgO.	Al₂O₃.	Fe₂O₃.
Yellow clay.	Digestion flask.	76.48	0.64	0.36	0.82	0.71	9.57	5.71
" "	Stoppered bottle.	76.78	0.58	0.39	0.80	0.72	9.48	5.60
" "	Covered beaker.	78.98	0.31	0.22	0.89	0.61	8.11	5.03
Red clay....	Digestion flask.	78.12	0.41	0.26	0.22	0.27	6.51	4.67
" "	Stoppered bottle.	78.44	0.46	0.20	0.18	0.30	6.20	4.59
" "	Covered beaker.	80.84	0.26	0.18	0.19	0.22	5.21	4.45
Sandy soil..	Digestion flask.	88.71	0.85	0.35	0.29	0.10	2.22	1.69
" " ..	Covered beaker.	88.98	0.76	0.32	0.26	0.08	2.32	1.56
Prairie soil .	Digestion flask.	75.80	0.39	0.18	0.50	0.63	6.42	1.91
" " .	Covered beaker.	77.01	0.22	0.16	0.44	0.58	5.27	1.81

Under the same conditions the digestion flasks and the glass stoppered bottles give practically the same results with the advantage as to rapidity and less liability of losses in favor of the digestion flasks. Both of these methods give higher results for the potash and the alumina than the covered beaker. This is due to the action of the acid upon the soils at a more uniform temperature and maintaining the acid at its initial strength. The result is that a larger quantity and a more constant amount of the complex silicates of potassium and aluminum are decomposed. That this is true can be shown by digesting these clay soils after the five days' action of the hydrochloric acid in the porcelain beaker with a fresh quantity of acid, when an additional quantity of potash, iron, and alumina is obtained. At what point should this action of the acid upon the soil be brought to a close, or should the digestion be continued until only a very small quantity can be dissolved by the acid? These points can only be decided by careful culture experiments, but it would seem more reasonable to allow the complete action of the acid rather than stopping it at some indefinite intermediate point.

With some soils, especially sandy ones, the differences are slight, while with other soils, especially refractory clays, the differences are quite large. When so much care is taken to adjust the strength of the acid to sp. gr. 1.115, equally as much care should be taken throughout the operation to retain the strength of the acid. This is accomplished by the use of the soil digestion flask.

PATENTS OF INTEREST TO CHEMISTS.

H. S. Blackmore first forms an alkali formate by the action of carbonic oxid upon a caustic alkali in a state of fusion, then continues the reaction so as to decompose the formate into a carbonate and set free hydrogen gas (497,700). To obtain pure carbon dioxid, Walter Walker passes the impure gas into retorts containing a solid carbonate which absorbs the gas forming a bicarbonate. Nitrogen and other gaseous impurities are removed by exhaustion; heat is applied to drive off the purified carbon dioxid, and the crystals of carbonate are re-obtained (496,546).

Herman Kropff (497,327) describes an improvement in the pasteurization of liquids. Charles Bullock (497,857) has an improved method for treating alcoholic liquors, as has also William Saint Martin (497,033). Charles Rettig has an apparatus for aerating, cooling, and clarifying liquors (498,571) and T. R. Timby places barrels of wines on trucks and runs on tracks with undulating rails in order to age the wines (496,759). E. Polgar obtains 497,814 on the manufacture of spirits from amylaceous materials and Otto Schweissinger (496,752) manufactures extract of hops by a new process.

George H. Smith has a method for making varnish (496,451). Ludwig Pflug patents a paint for ships (496,895), which contains hydrazin and its salts, and W. N. Blakeman, Jr., has a process for utilizing metallic and earthy oxids and salts as pigments or paints (496,990), by combining with some salts capable of absorbing carbon dioxid when the pigments are applied.

M. B. Church mixes gypsum with glue as it comes from the rendering tank without drying as a process for making "retarded gypsum" (497,947), and 497,948 is a process for manufacturing gypsum compounds, which consists in mixing the gypsum in a dry, pulverized condition, with the retarder in a hot liquid condition. A. T. Denison obtains pulp from vegetable substances by the action of an alkaline nitrate under pressure and heat (496,400.)

A. D. Little has a process for tawing hides by forming in the skins a chromium compound, and then subjecting to a bath

of sodium sulfid and hydrochloric acid (498,067). W. M. Norris, to accomplish the same purpose, first dips in a bath of potassium bichromate and hydrochloric acid, and then treats with a solution evolving hydrogen sulfid (498,077), while 498,214 is also for the same object.

Walter D. Field has a "process for producing sulfuretted oils and products thereof" (498,162). The non-drying glycyl or glyceryl ethers of the unsaturated fatty acids are combined with benzine or its equivalent, then chlorid of sulfur is added at a temperature less than 40° C. and when combination is effected, chlorin, free acid, and benzine, or its equivalent, is driven off by heat. Charles Toppan treats mineral or vegetable oils to the action of gases evolved from salt, metallic zinc, and sulfuric acid (498,588). Messrs. Benoit and Vila separate olein or stearin from suet by liquefying tallow, adding manganese to clarify it, allowing to settle, decanting the upper portion and heating this. After adding cream of tartar it is again allowed to settle and decanted and finally heated until olein and stearin are separated (498,375). Wm. N. Blakeman, Jr., thickens drying oils by adding a mixture of cotton-seed oil and a metallic soap (496,988). Mr. Blakeman also has three other patents on processes for imparting drying properties to oils, viz. : 496,991, 496,989, and 496,987.

As usual, there are a number of new dyes. 496,392 is a blue tetrazo dye, patented by J. Bammann and M. Ulrich ; 496,435 is another blue dye, the discovery of Oscar Nastvogel; and 497,032 is an orange azo dye, credited Christian Rudolpho. Emil Von Portheim patents a glycine dye, formed by the addition of a tetrazo compound of a diamine with a glycine (498,303), and Jacob Braek obtains a blue dye by heating an amine of the fatty series with a gallocyanine (497,114). Hugo Hassencamp describes a triphenyl methane dye (498,471), and Philip Ott has two new diazo dyes, one a reddish blue (498,405), the other a greenish blue (498,404). Ernest Bonsier uses alcohol, ammonia, carbolic acid, naphtha, and oleic acid for a mordant (497,229).

Harriet Carter patents "hard coal ashes, fine hard coal, white sand, fire-clay, and fine salt, mixed with water," as a composition for saving fuel (497,627); C. Cronin uses a combination of "culm,

wood-pulp, ground limestone and crude petroleum " for a fuel
(498,629). "Ground ocher, cotton-seed oil, and liquefied resin"
is a compound for preserving wood, patented by W. A. Gayle
(497,471), and Ludwig Frorum adds hazel-nut flour to fari-
naceous products to preserve them (496,780). Jacob Ziegler
has a new antiseptic, a quinolin compound, (497,740), and H.
P. Weidig employs a solution of bromin and potassium perman-
ganate for a disinfectant (497,082). An antiseptic embalming
fluid, containing "bisulfite of potash, soda or lime, sulfite of
aluminum, and sulfite of lime, dissolved in an aqueous solution
of sulfurous acid" is patented by Max Huneke (498,350) and
Otto L. Mulot has a medicinal composition (496,694), the elec-
trolyzed distillate from a mixture of a dozen ingredients.

R. M. Shearer anneals aluminum wire, subjects blanks to a
bath of sodium hydroxid, a water bath, a nitric acid or potas-
sium chlorate bath, and a second water bath in his process for
"pencil and art of making it," (497,350). F. P. Harned makes
cast astringent pencils (497,659) of aluminum sulfate by reduc-
ing material under steam pressure, adding at intervals aluminum
sulfate in solution, and casting in a greased appliance.

Robert J. Kennedy has a hydraulic amalgamator (498,979).
Orrin B. Peck has eight patents on an ore separator (499,342-349).
'C. E. Seymour has a concentrator (498,823). John M. Finch
has a separator (499,915) and R. H. Sanders and Charles T.
Thompson have a magnetic separator (499,253). G. W. Nixon
patents a new coke oven (499,565), and Jacob Reese has a pat-
ent basic lining (499,248), a highly burned non-calcareous com-
pound of magnesia and tar, externally glazed. E. D. Kendall
uses a mixture of hyposulfites and ferricyanids and water for a
composition of matter to extract precious metals from their ores
(500,137), while John A. Frey uses carbonated soda-ash, silica,
sand, and pulverized sal-ammoniac, mixed in the dry state, for the
purification and separation of metals and their alloys (499,018).

John M. Hartman has two patents, one (500,386) on an iron-
notch for blast-furnace, and the other (500,387) on a blast-
furnace. Martin V. Smith reduces zinc ores by passing the
fumes over batches of ores in a separate condenser (500,436).
Charles C. Bartlett smelts nickel ores with a flux of niter cake,

salt-cake, nitrates or carbonates of alkaline bases, separates out buttons rich in sulfid of nickel, by specific gravity and repeats the smelting operation to obtain nickel sulfid (499,314)   F. W. Martino forms alloys of nickel and other metals by a peculiar process (499,559). F. R. Carpenter treats ores as follows: First mixes with a flux containing magnesia to form a light slag of definite proportion; second, adding sulfid of iron matte-forming materials free from copper and lead; third, heating, when the heavy iron slag will sink, taking the precious metals; fourth, adding lead to the molten sulfid (499,318).

Michael A. Goloseieff utilizes gelatine refuse or broth from evaporating to 27°–28° B., adding quick lime, allowing mass to expand and dry, and grinding (500,100). Eduard Rauppach and Leopold Bergel heat a mixture of curds and water to 104° F., add an alkali to precipitate the casein, and after separating the latter, heat it with an alkaline solution to 90°–110° F., in their process for making glue (500,428).

Carl Rach has a patent on the preparation of wort from Indian corn (500,294). Wm. E. Bradley has an improvement on the manufacture of whisky (499,316) and James A. Tilden patents a process of malting (500,305).

Etienne Watel extracts perfume, essences using a patent apparaatus (498,830). C. J. Delescluse, to bleach raw cotton, treats it in a bath of a chlorid solution, water, grape sugar, and sulfuric acid (499,184). Victor G. Blaede has a process for dyeing and printing (499,649); George Donaldson, a scheme for printing on cotton (499,161); and Otto P. Amend, a process for dyeing anilin black (499,410). W. T. Whitehead has several related patents (499,687–692 inclusive) of interest to dyers in which a zinc composition is the active element.

J. Bammann and Moritz Ulrich have several new blue tetrazo dyes (499,198, 498,759, 498,873, and 498,874) and Emil Meyer (499,243), and Carl Drusberg (499,216) have each a blue dye.

Prosper Monnet patents a process for making anisolin (499,927). Meinhard Hoffman patents his plan for forming naphthylene-diamin-disulfo-acid (498,882), and 499,301 is a process for making derivatives of amido-crotonic acid, invented by L. Lederer.

G. W. Scollay heats vegetable oils under pressure until the

natural color is discharged and then at once reduces the temperature before color is recovered, to refine the oils (498,821) and he also has a plan for treating cotton-seed oil (498,822) which consists in heating until vapor heavier than air is given off and then removing vapor before it is converted into vapor lighter than air. Herman Frasch has a compound for purifying Canadian or similar petroleum which contains metallic oxids as lead or copper (500,252). Edwin Tatham has a method for making gas (499,483), and 499,994 and 499,995 are granted Henry C. Higginson on the manufacture of whiting.

George H. Blake uses "wood-tar, rosin, and pulverized plumbaginous slate" as a composition for roofing (498,840), while A. Monroe incorporates the following for the same purpose, "Portland cement, sand, plaster of Paris, crude petroleum, turpentine, salt, and water" (500,024). James E. and G. H. McAlpine use for a fire or water proof paint, a mixture of coal-tar, crude petroleum, benzine, resin, sulfate of zinc, sal-soda, and linseed oil (500, 346). "Hydromagnesite, oxalic and boracic acids and mother liquor of sea-water with sand, fiber and an oleaginous substance" is what Hugo Gallinowsky names as an artificial stone composition (500,485).

Enos A. Bronson prepares a finish for plastering by mixing lime, gypsum, white sand, soap-stone or talc, and china clay or kaolin with enough water to form a pasty mass, adding alum and borax, drying, grinding, and adding to the mass calcined gypsum and white sand (499,710).

August Viner uses saltpeter, borax, glycerin, and water as a compound for glazing collars and cuffs (499,685), and "whiting, ammonia, kerosene oil, coal ashes, and water" is what is claimed by Dora A. Smith for a silver cleaning composition (499,401). "Oil and sulfur boiled together, turpentine and salt," Walter E. Rohner combines for wood-polishing (498, 961). Carbon and tar pressed and baked in place form a composition for attaching anti-friction linings or facings, (K. W. Hedges, 499,111). E. Schloesing uses "spent oxid" from gas works or "Laming mixture" freed from cyanids and tobacco for an insecticide (498,819). Robert W. Johnson has two patents on a sulfur candle (499,324 and 499,325), and Edward

Watson uses oxid of chromium as the active agent for fumigations (499,407). John Rowbotham has a moulding compound (499,753), and J. de S. Brown uses bitumen and sulfur with fine filling as lead protoxid and gum camphor, incorporated with bitumen and toughened and hardened by heat as a substitute composition for hard rubber (499,354).

Jacob Mellinger has a soap for removing hair from skins (499,134) and H. F. Dietz protects his method of carrotting and dyeing fur by 498,910. 500,535 is granted Anatole and Ernest des Cressonieres for a process of and apparatus for the manufacture of "kneaded and agglomerated soaps," and Max. Güttner adds to molten tin or an alloy of tin and lead an oxidizing substance, removes scum and repeats this operation several times prior to casting in his process for preparing solder (500,125).

[The specification and drawing of any U. S. Patent in print may be obtained from the publisher of this Journal. Applications must be accompanied in all cases by twenty-five cents for each patent specification wanted. BE CAREFUL TO WRITE THE NUMBER LEGIBLY.]

NEW BOOKS.

LECTURE NOTES ON THEORETICAL CHEMISTRY. BY FERDINAND G. WIECHMANN, PH.D. 12 mo. 225 pages. New York: John Wiley & Sons. Price, $2.50

A book evidently written for class use. The chapter headings are: Introductory; Specific Gravity; Chemical Nomenclature and Notation; Atoms, Atomic Mass, Valence; Chemical Formulæ; The Structure of Molecules; Chemical Equations and Calculations; Volume and Weight; Relations of Gases; The Periodic Law; Solutions; Energy, Chemical Affinity; Thermal Relations, Thermo-Chemistry; Photo-Chemistry; Electro-Chemistry; Bibliography. The author says something in each sentence and although the book is of moderate size it contains a great deal of matter. In chapter III Dr. Wiechmann gives a brief but interesting account of the systems of chemical nomenclature and notation from the earliest times to the present date, concluding the chapter with an account of the methods of spelling and pronunciation adopted by the American Association for the Advancement of Science in 1891. The book doubtless contains some mistakes and omissions and some topics are given too

little, others too much space, but it is nevertheless a good book
to give to a student—for he will be able to understand it, and
can then use the Bibliography to advantage. At first sight the
omission to refer to separate papers in verification of the state-
ments made by the author seems a mistake, as such references
would be invaluable to one who wished to study the subject
exhaustively ; but the compass of the book doubtless prevented
this.   E. H.

ALEMBIC CLUB REPRINTS, NO. 1 ; EXPERIMENTS UPON MAGNESIA ALBA,
    QUICK-LIME AND OTHER ALCALINE SUBSTANCES. BY JOSEPH BLACK,
    M. D., PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF EDIN-
    BURGH (1766–1797). 12 mo., 47 pp., Edinburgh: Wm. F. Clay, 3s. 6d.
    with postage.

The Alembic Club is the name of the Edinburgh University
Chemical Society, which have undertaken a useful work of
which this is the beginning. Black is one of the workers whose
papers will always be worth reading and this reprint will be very
useful in spreading the knowledge of what he did. Too few of
the moderns are acquainted intimately with the work of their
predecessors—men like Black, Cavendish, Bergmann, Scheele—
who did so much with so little. This booklet is nicely printed in
old style type and on good paper, retaining the original spelling.

NOTES.

Detection of Phenacetin and Acetanilid.—In the February, 1893,
number of the JOURNAL OF ANALYTICAL AND APPLIED CHEM-
ISTRY, on page 82, there is a paragraph relating to certain char-
acteristic tests on phenacetin and acetanilid. It reads as follows:
" As previously mentioned, the formation of alcohol through treat-
ment with caustic potash serves to distinguish phenacetin from acet-
anilid. Another test useful also in detecting small quantities of
acetanilid in presence of phenacetin is to treat the mixture with
caustic soda or potash in the presence of chloroform, when, if acet-
anilid be present, the characteristic odor of 'isonitril' is given off."

I have no doubt as to the author's good intentions, but as a
matter of fact, the above tests fail to distinguish acetanilid from
phenacetin.

Repeated attempts to obtain alcohol by boiling phenacetin with

caustic potash were unsuccessful. Moreover, I have been unable to find any law in aromatic organic chemistry that would suggest the possibility of any such reaction.

If any reaction at all takes place, the probability is that the acetyl radicle, and *not* the alkyl group, is attacked.

As to the isonitril or carbylamin reaction, both acetanilid and phenacetin give it, for these compounds belong to that class known in organic chemistry as *Primary Amines* (general formula $= R—NH_2$) to which the isonitril reaction is common. Hence, the worthlessness of the isonitril reaction to distinguish phenacetin from acetanilid.

In applying the isonitril test to phenacetin, it is necessary that the drug should be in powdered form, since the compressed tablets, as sold by the druggist, offer a certain amount of resistance to solution and thus hinder the reaction.

Concerning the melting point the writer found that *pure* phenacetin crystallized *from alcohol* melted at a temperature less than 100° C. while the *same* sample crystallized from *benzene* gave the proper melting point, 135° C. F. S. HYDE.

Bibliography of Alcoholic Fermentation.—Dr. H. Carrington Bolton, chairman of the Committee on Indexing Chemical Literature of the American Association for the Advancement of Science, sends the following note with a request for its publication:

The writer wishes to call the attention of fellow-workers to the fact that he is preparing a bibliography of alcoholic fermentation with special reference to vegetable physiology. He will be very glad to receive notes concerning the literature of this question from botanists, chemists, and physiologists in this country, who are interested in having bibliographies of this kind complete as far as possible.

J. CHRISTIAN BAY,
Missouri Botanical Garden, St. Louis, Mo.

Colloidal Barium Sulfate.—By mixing 120 parts of a forty per cent. barium acetate solution with eighty parts of a sixty per cent. alumimum sulfate solution Georg Buchner finds (*Chemiker-Zeitung*, 1893, 878) that a thick, transparent, gelatinous mass is formed. On diluting this with water barium sulfate separates. If the gelatinous mass is brought on a filter the filtrate gives barium sulfate on dilution. The residue on the filter becomes milk white after standing.

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